AECV92-R1

The Analysis of QA/QC Results for AEC E128.0 Analytical Method for Adsorbable Organic Halide (AOX)

Alberta
ENVIRONMENTAL CENTRE

92-04504/

THE ANALYSIS OF QA/QC RESULTS FOR AEC E128.0 ANALYTICAL METHOD FOR ADSORBABLE ORGANIC HALIDE (AOX)

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NOVEMBER, 1991

This Report may be cited as:

C. Ian Johnson, Tonya Lam and John Kirtz. The Analysis of QA/QC Results for AEC E128.0 Analytical Method for Adsorbable Organic Halide (AOX). Vegreville, AB. Alberta Environmental Centre. AECV92-R1. ISBN 0-7732-0914-X.

ABSTRACT

The quality assurance quality control (QA/QC) program for AEC Method E128.0 for adsorbable organic halide (AOX) in bleached kraft mill effluents (BKME) is discussed and evaluated in this report. Potential causes of error and the good laboratory practices (GLP) used to avoid them are outlined and discussed. Quality control test data gathered over a fourteen month period are evaluated. The method blank and daily calibration factor were found to have very little effect on method performance but the within day variance of these test results related directly to method performance. Data from duplicate analysis were analyzed and the method detection limit (MDL) of the analysis was found to be approximately 0.005 mg/L AOX as chloride. The estimated standard deviation of BKME diluted 100 times was 0.23 mg/L AOX as chloride. This method was found to be appropriate for both BKME and river waters receiving BKME. Analysis of 2-chlorobenzoic acid spikes revealed that the method efficiently recovered this compound from the matrices encountered.

ACKNOWLEDGEMENTS

The authors wish to acknowledge Dr. R.D. Smillie, Head, Research and Methods Development Branch, of the Alberta Environmental Centre, for his support and assistance in the in the preparation of this report and Dr. L.Z. Florence, Head, Biometrics Section, of the Alberta Environmental Centre, for his valuable advice on statistics and the presentation of statistical data.

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The Analysis of QA/QC Results for AEC E128.0 Analytical Method for Adsorbable Organic Halide (AOX)

C. Ian Johnson[a], Tonya Lam[a], and John Kirtz[b]

Introduction

Release of organic halide containing compounds to the environment has become a concern during the last two decades. These include both compounds used, or previously used, industrially such as polychlorinated biphenyls and pentachlorophenol, and compounds formed as byproducts in industrial processes involving the use of elemental chlorine. A large source of these latter compounds is the chlorine bleaching of kraft pulp.

There are numerous methods to determine the concentrations of organic halides in industrial effluents and the environmental samples but none is universally applicable. These methods include: Total Organic Halide (TOX)[1] for the determination of the dissolved organic halide adsorbed on activated charcoal under specific conditions; Total Organic Chloride (TOCl)[2] for the determination of organic chloride absorbed by the polyamide resins XAD-2 or XAD-4; and Adsorbable Organic Halide (AOX)[3] for the determination of total organic halide in an aqueous sample associated with the suspended solids and organic halide in solution and adsorbable on activated charcoal. This last method is applicable to pulp and paper mill effluents and internal process filtrates.

This report presents and discusses the method validation data and quality control data for the Alberta Environmental Centre method E128.0 for the determination of AOX (Appendix 4). This method was designed specifically for biologically treated bleached kraft pulp mill effluents but it has also been used to generate high quality results in the analysis of receiving waters of these effluents.[4,5]

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AOX, like other organic halide methods, is a sum parameter method. It does not measure the concentration of specific compound or type of compound, but measures the concentration of all organically bonded halide. The nature of the chlorinated compounds contributing to the AOX varies considerably as follows: molecular size; toxicity; bioconcentration and bioaccumulation factors; and chemical stability and persistence in the environment. Great caution must be used when drawing conclusions or making decisions based solely on AOX data. It is best to use AOX as a "surrogate parameter", which indicates the presence of chlorinated compounds. If AOX is present in a sample, further analysis, using methods appropriate for the compounds of interest, should be undertaken. It must be noted, however, that it is entirely inappropriate to use AOX as a screening or surrogate analysis for polychlorinated dibenzodioxins (PCDD) and dibenzofurans (PCDF) present in very low concentrations. AOX analysis is simply not sensitive enough.

General Method Description

Presented here is a general description of the method. Appended to this report is the AEC Analytical Method E128.0 for AOX. This method can be separated into three distinct operations shown in Figure 1; the adsorption on granular activated carbon (GAC); the isolation of the GAC and suspended solids by filtration; and the determination of the chloride by oxidative pyrolysis/micro-coulometric titration.

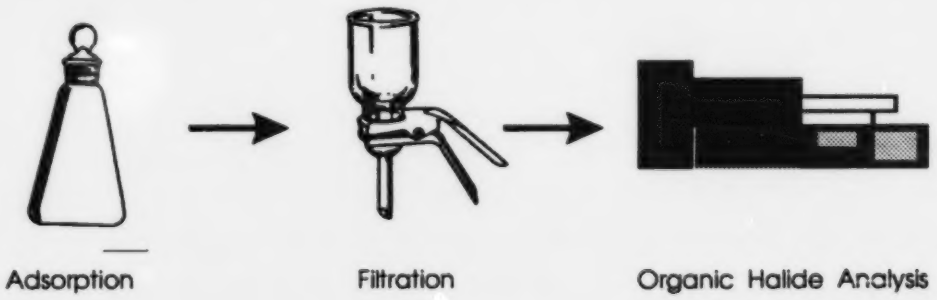

Figure 1 AOX Analysis Operations.

In the first operation, the adsorption onto GAC, sample are diluted with acidified (HNO_3) aqueous sodium nitrate and shaken with GAC in a sealed conical flask. The organic compounds present, including the

organic compounds containing halogens, are adsorbed on the GAC. An aqueous sodium nitrate is used to prevent the adsorption of inorganic chloride ions as nitrate ions displace any chloride ions adsorbed to the GAC.

The GAC and suspended solids are collected in the filtration operation. Following the adsorption operation, samples are filtered through a polycarbonate membrane filter (0.4 μm pore size) and rinsed thoroughly with a nitrate solution to displace any remaining bound inorganic chloride. The filter membrane and all the collected material are set aside for organic halide analysis.

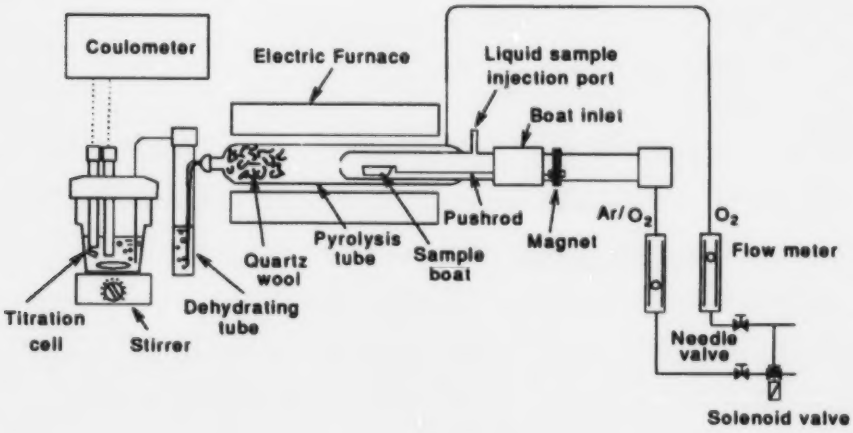

Figure 2 Mitsubishi TOX-10 Analyzer used for AOX analysis.

The organic halide analysis involves the conversion of organic halide to hydrogen halide by oxidative pyrolysis followed by the determination of the halide by microcoulometric titration. The instrument used for this operation is shown in Figure 2. The filter membrane and collected material are pyrolyzed under an oxygen atmosphere at 950°C converting the organic halide to hydrogen halide which exhaust gases sweep through a dehydration tube, and into the titration cell. Here the amount of halide produced is determined by microcoulometric titration. This is similar to the classical silver/silver chloride

potentiometric titration of halide, except silver ions are generated electrolytically at a silver electrode. This technique is more sensitive than the classical silver nitrate titration, as the amount of silver ion generated can be very small yet it can be measured very accurately. Results are quantified as chloride.

Analytical Error and Method Performance

As with all analytical methods, there are measurement errors in AOX analysis. The potential sources of error associated with each operation are listed in Table 1. Errors due to organic chloride contamination or the titration endpoint error are constant in sign and magnitude for all samples, and are unaffected by concentration of AOX in sample. In this text, these errors will be referred to as absolute errors. The magnitude of error resulting from errors in dilution, pipetting, gas leaks, and the inefficiency of generation of Ag^+ ions are proportional to the AOX concentration of the sample. In this text these errors will be referred to as relative errors.

Table 1 Potential sources of error in AOX analytical method.

Operation	Error	Cause or Source of Error
Sample Adsorption	Organic Chloride Contamination	- contaminated glassware. - contaminated granular activated charcoal. - halide present in chemical reagents and dilution water.
	Measuring Errors	- pipetting and dilution errors in preparation of sample for adsorption.
	Incomplete Adsorption of Sample	- excess amount of dissolved organic material in sample saturating GAC.
Filtration	Organic Chloride Contamination	- contaminated glassware. - contaminated filter membranes. - contaminated air drawn through filter.
TOX Determination	Incomplete Conversion of Organic Halide	- contaminated or pitted surfaces in pyrolysis tube.
	Incomplete Transfer of Hydrogen Halide to the Titration Cell	- leaks at the pyrolysis tube/dehydration tube joint.
	Titration Errors	- inefficient Ag^+ generation due to spent electrolyte or a contaminated generator electrode. - titration end point error.

The errors associated with the method can be further divided into two other separate components: a systematic component which remains constant, and can include both absolute and relative error; and a random component which varies with each determination. The systematic component of error effects the accuracy of the analytical method. In AEC Method E128.0 for AOX, blank subtraction and a calibration factor are used to correct results for the systematic component of the absolute and relative error respectively.

Results cannot be corrected for random component of error where the sign and magnitude of this error may vary randomly with each measurement. The analytical results will be randomly scattered around the true value. In most chemical analyses the distribution of these errors approximates the normal distribution, the probability density function being:

$$p(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{-(x-\mu)}{2\sigma^2}} \qquad (1)$$

where p(x) is the probability density function of result x, μ is the true mean, σ is the true standard deviation and σ^2 is the true variance of the underlying population sampled by the test. Given μ and σ the probability (typically 0.95 or 0.99) of a result x falling in a range x_1 to x_2 can be calculated as the integral of equation 1 between x_1 and x_2. Conversely, for any x, a range with a probability of containing μ may be calculated given σ. As the true value of σ is not know, estimates using the standard deviation, s, of the results of repeated analyses ($n \geq 7$) of a dilute sample, and the Student t distribution are used to calculate the range. The width of this range is a measure of the precision or reproducibility of the analysis.

The precision, or standard deviation also defines the minimum reliable result which can be reported using the analysis. The method detection limit (MDL) is the lowest value which can be reported with a 99% confidence that the true value is greater than zero. It is generally calculated as three times the standard deviation of low level analysis (estimated with at least 6 degrees of freedom). In the case of this AOX method, where the MDL defines the sensitivity of the test, it is crucial to minimize method standard

deviation and to control it on a daily basis. This is the main purpose of the Quality Assurance / Quality Control (QA/QC) program.

Quality Assurance / Quality Control (QA/QC) Program

There are two major components of this laboratory's QA/QC program: the documentation and use of **good laboratory practices** (GLP); and the daily performance of routine tests monitored by Shewart control charts. Another minor component is the annual review of QA/QC test results.

GLP's are *rigid* procedures designed to minimize error, give a high degree of reproducibility to analysis and ensure the **safe** implementation of the analysis. These procedures are contained in the method or in relevant standard operating procedures. These practices cover procedures such as: maintenance of the instrument and the equipment; preparation of glassware; preparation and handling of standards; and handling of samples.

Specific to this analysis is another element of GLP, the replicate analysis of samples at different dilutions. This test is used to verify that the GAC has not become saturated and its capacity exceeded. Although this replicate analysis does minimize variation, the primary purpose is to validate each analysis.

Five routine daily tests are used to monitor the performance of the analysis. These specific tests were selected because specific test failures also indicate the remedial action to be taken. Results of five tests are used to determine AOX accuracy and precision:

1 Measurement of analytical blanks - used to monitor background (contamination) and background variation.
2 Analysis of calibration solution - used to determine the instrument response factor and the variation in response factor between analyses.
3 Analysis of samples in duplicate - used to monitor the reproducibility or precision of the method. The method variation or standard deviation can also be calculated from the duplicate results.
4 Analysis of samples fortified with 2-chlorobenzoic acid - used to monitor method accuracy.

5 Analysis of QCA/QCB check standards - the analysis of two standards, one 70% of the analytical range and one 20% of the analytical range. The sum of the two results is used to monitor the calibration intercept and the difference of the two results is used to monitor the calibration slope.

Shewart control charts are used to monitor the results of these daily tests. A typical Shewart chart is shown in Figure 3. The mean, x, and the standard deviation, s, of quality control (QC) test results are plotted on a daily basis. Warning limits and control limits for test results are established for test results and are drawn as dashed horizontal line on the charts. In our implementation, these limits are set such that the probability of a result falling beyond the warning limit is <0.05 and of falling beyond the control limit is <0.01. Results which lie outside these limits indicate that the parameter monitored is out of control and remedial action is necessary.

Monitoring of QC test data using Shewart control charts assumes that the population test data are drawn from one homogenous distribution and that it is possible to calculate confidence intervals. If this is not the case it may not be possible to base warning and control limits on confidence intervals. More importantly, the results of the analysis will not be reliable.

The population of test results is expected to be normally distributed although other distributions are possible. When the test results are normally distributed the distribution of the daily test variances is related to the χ^2 distribution by the equality:

$$s^2=\frac{\chi^2\sigma^2}{(n-1)} \qquad (2)$$

where σ^2 is the true variance of the underlying population sampled by the test, s^2 is the observed variance, n is the number of tests, and n-1 is the number of degrees of freedom. The probability frequency function of the χ^2 distribution is:

$$p(x)=\frac{1}{2^{(n-1)}\Gamma\frac{(n-1)}{2}}x^{(\frac{n-1}{2})-1}e^{\frac{-x}{2}} \qquad (3)$$

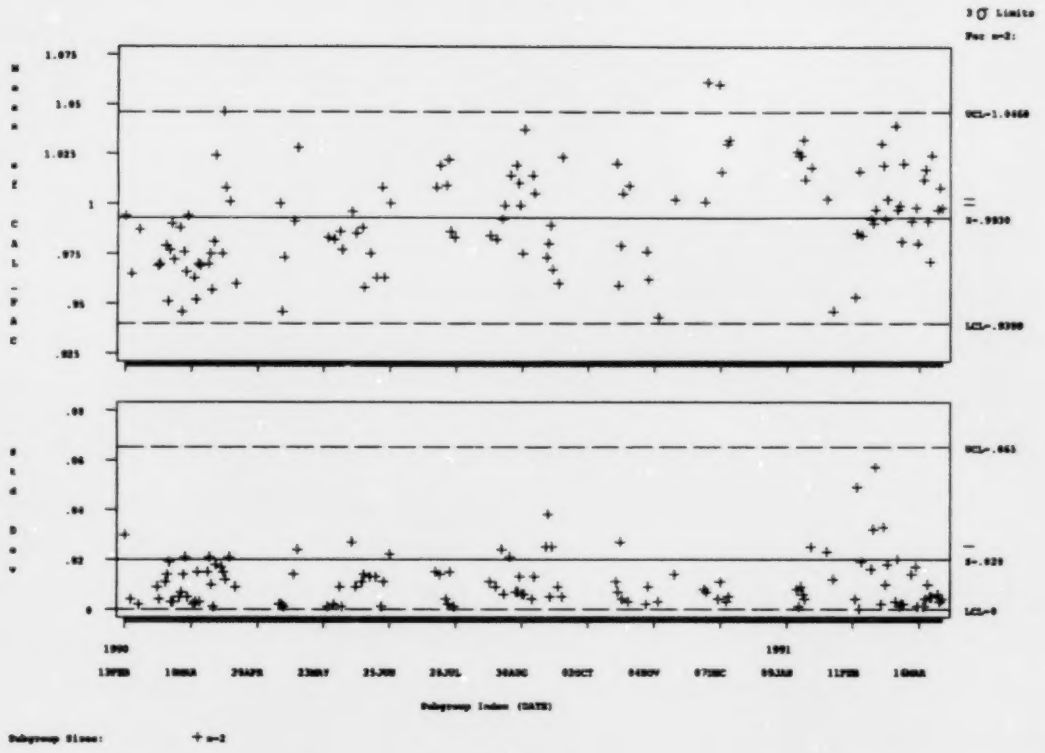

Figure 3 Shewart control chart of calibration factors.

where the only variable is the number of degrees of freedom (n-1). When test results are normally distributed, F distribution tables may be used to calculate warning and control limits for variance and/or standard deviation.

Materials and Methods

AOX Quality Control Data

A Mitsubishi TOX-10 organic halide analyzer was used for all AOX measurements. AEC Method E128.O and the equipment and materials specified therein were used for all AOX quality control tests. Quality control data were generated between February, 1990 and April, 1991 (see Appendix 1).

Analysis of Quality Control Data

Analyses of data were done using PC/SAS® ver. 6.04 run on a Fujikama 386 personal computer with a math coprocessor. Outliers in the AOX control data, listed in Appendix 1, were removed based on a 99% confidence interval prior to any analysis.

PROC CAPABILITY procedure of SAS/QC® was used to fit distributions to QC data sets. This software uses a maximin likelihood fitting algorithm[6] and tests the fit using the χ^2 goodness of fit test.[7] Standard test data were fit to normal distributions and the variances of daily tests were fit to γ distributions constrained to χ^2 type distributions with the appropriate number of degrees of freedom. Spearman and Pearson correlations and probabilities between data sets were calculated using the PROC CORR procedure of base SAS®. SAS® source code used is listed in Appendix 2. The results are listed in Appendix 3.

Results and Discussion

The complete set of QC results generated between February 1990 and April 1991 are presented in Appendix 1. These results were evaluated as they were generated using Shewart control charts, as part of the laboratory's QA/QC program. The analysis presented here deals with the distribution of the populations of the results. Distributions fitted to the QC data are summarized in Table 2. The μ and σ of the fitted normal distributions and estimated means and standard deviations of χ^2 type distributions are listed along with probabilities for χ^2 goodness of fit tests and Shapiro Wilk W tests.[7,8]

The Shapiro Wilk W test is used to test if a set of data is normally distributed; it does not test the specific distribution with μ and σ specified. The null hypothesis of the test is "the data are sampled from a normal distribution", and it is rejected with a probability of 0.05 or lower, there being a low probability of falsely rejecting the null hypothesis (95% confidence level). The χ^2 test is used to test the specific fitted distribution. The null hypothesis, being "the fitted distribution is the distribution of the data", is rejected

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approximate the distribution tested. The fits of data using other distributions were only tested with the χ^2 test as the Shapiro Wilk W test is not applicable to non-normal distributions. All test results were fit to normal distributions and test variances were fit to γ distributions constrained to a χ^2 type distribution with n-1 degrees of freedom. These fitted distributions differ from χ^2 distributions only in scale. They have been rescaled so that the distribution mean is the variance (s^2), rather than the number of degrees of freedom.

Calibration Factor

The frequency distributions of calibration factors and the variance of calibration measurements distribution are shown in Figures 4 and 5 respectively. The calibration factors are normally distributed, as is indicated in Figure 4 and by the probabilities of the Shapiro Wilk test and the χ^2 goodness of fit test in Table 2. The variance of calibration factor measurements follow a χ^2 type distribution (1 degree of freedom), shown in Figure 5, and by the probabilities of the χ^2 goodness of fit test. This indicates calibration factor measurement is a random variable, distributed about a true value μ, with a true variance σ^2. The variance can be estimated with s^2, the mean of estimated mean variance data. This variance however is significantly less than that observed for the calibration factor data.

The variance of measurement is constant over time. The two sources of random error contribute to this measurement variance are: the measuring error of the addition of calibration solution with *via* micro syringe; and error in the instruments determination of the added calibrant. We believe the former to be responsible for over half of the variance of these measurements.

The larger variance of the calibration factor data comprises this measurement variance and variance from other sources. The contribution of the measurement variance is small. The variance in the daily estimate of the calibration factor is the variance of the measurement divided by 2, as the estimate is the average of two measurements. From the variances in Table 2 it can be seen that the variance in measurement accounts for approximately 15% of the variance in the distribution of calibration factors (the square of the calibration factor standard deviation).

Table 2 Results of the fits of test results and variances to statistical distributions.

Test Parameter	Distribution	*n*	μ	σ	Estimated Mean	Estimated Std. Dev.	χ^2: Prob.	Shapiro W: Prob.
Calibration Factor	Normal	118	0.993	0.025			0.476	0.205
Calibration Factor Variation	Constrained γ	118			0.0001735		0.305	
Method Blank	Normal	116	0.429	0.111			0.002	0.043
	Log Normal				0.429	0.115	0.008	
	γ				0.428	0.111	0.015	
Method Blank Variation	Constrained γ	118			0.006574		0.289	
Recovery of 2-Chlorobenzoic Acid	Normal	77	98.62	3.57			0.647	0.925
Squared Differences of Duplicate Analyses								
< 5 μg Range	Constrained γ	64			0.05386		0.399	
5 to < 15 μg Range	Constrained γ	30			0.10887	0.358		
QCA + QCB	Normal	33	39.18	1.23			0.557	0.858
QCA - QCB	Normal	33	19.91	1.00			0.047	0.027

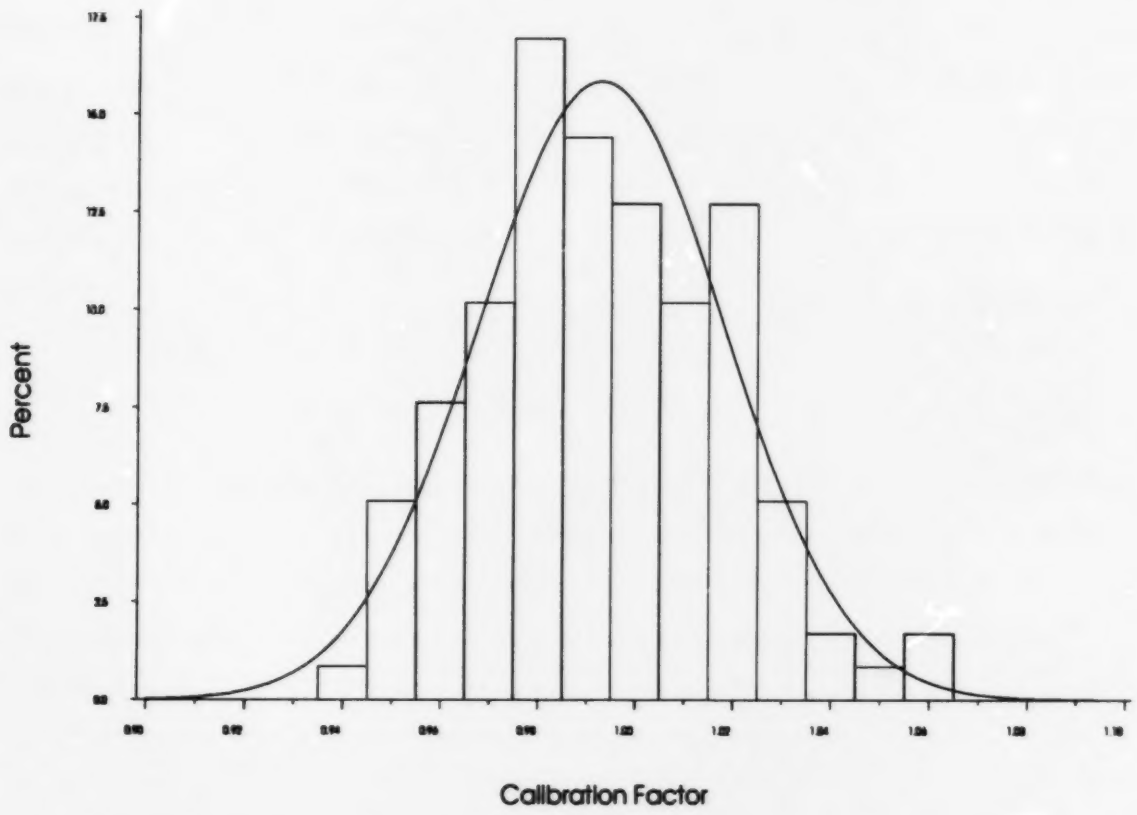

Figure 4 Calibration factor distribution and fitted normal distribution.

Furthermore, the variance of measurement is independent of the daily estimate of the calibration factor. Figure 6 is a scatter plot of the data ranks of the calibration factor vs the rank of the variance of measurement of calibration factor data sets. They appear to be uncorrelated. This is supported by the Spearman rank correlation coefficient of –0.035 for the two data sets which does not differ significantly from zero (probability ≥ 0.702).

While the true variance of the measurement of the calibration factors is constant and independent of the calibration factor, the true value of the calibration factor is a normal random variable changing on a day to day basis, with its own variance, 7 times that of the measurement variance. These daily changes are the result of the small changes in instrument performance which accompany the daily instrument maintenance, startup and shutdown. This has important implications in the interpretation of QC results

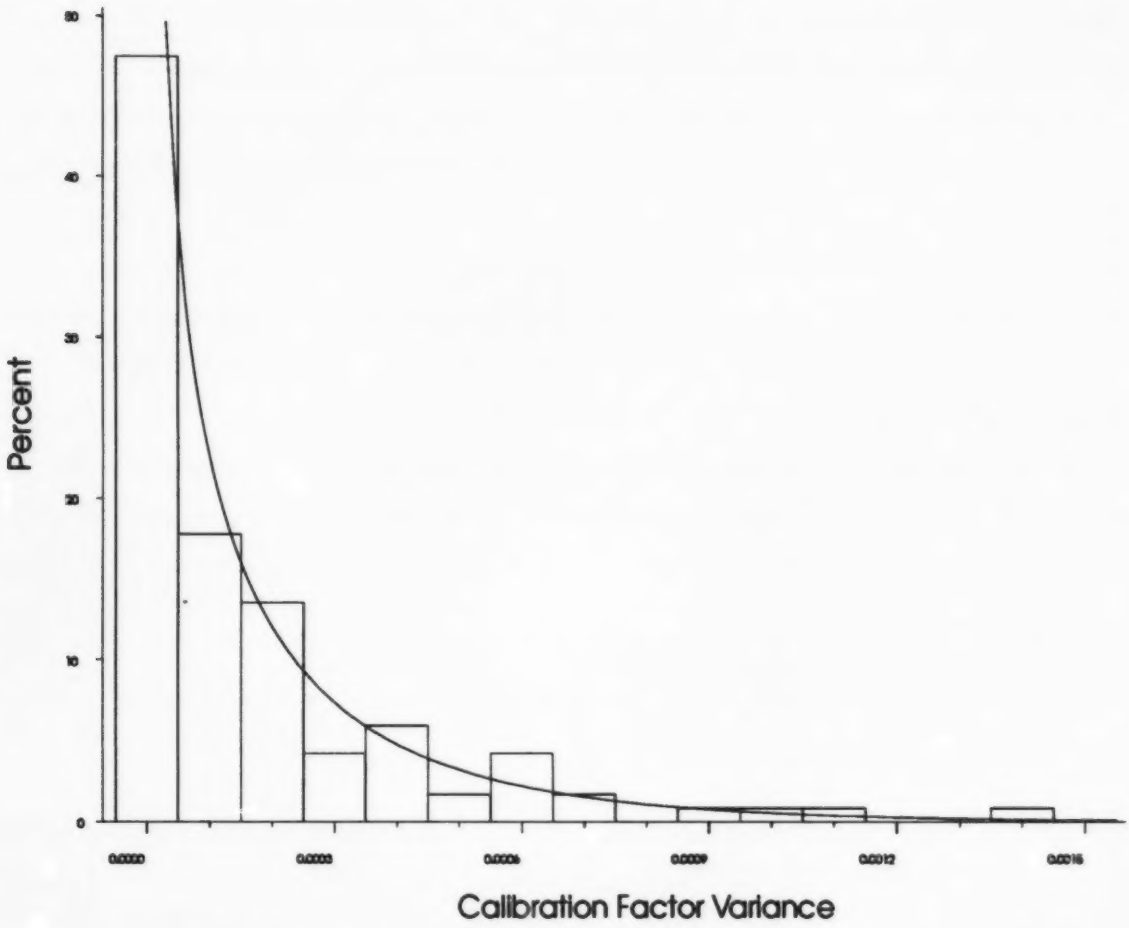

Figure 5 Distribution of variance of calibration factor measurement variance and fitted χ^2 type distribution (1 degree of freedom).

and their use in the optimization of method performance.

The variance in the measurement of the calibration factor is the variance of instrumental determination of halide and hence is part of the variation in the measurement of AOX. It is very important to monitor and control this variation. The random daily changes in calibration factor do not affect the results generated by the method as they are compensated for in the calculation of AOX.

The calibration factor is a much less precise parameter to control the analysis with but can be used to judge the state of the instrument and to determine when maintenance is necessary. Tight control limits

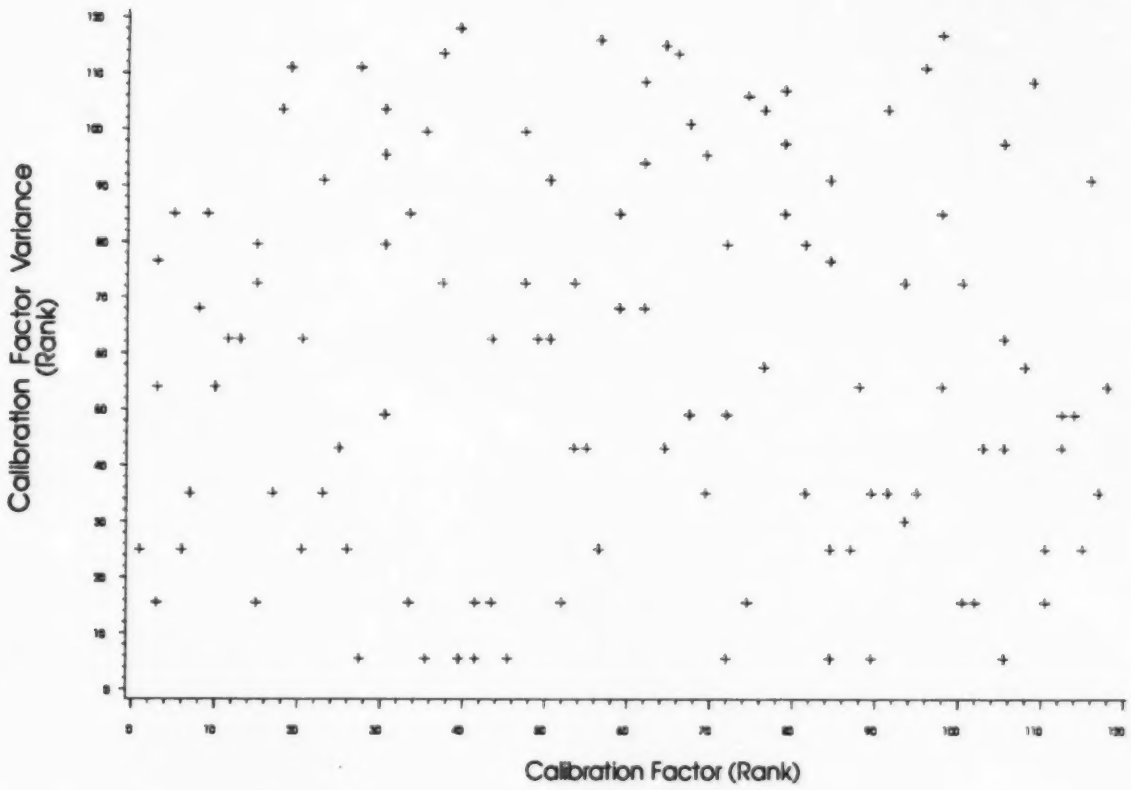

Figure 6 Scatter plot of rank of the variance of the calibration factor measurement versus the rank of measured calibration factor.

are not necessary for this parameter, and could result in needless shut downs. For this reason calibration factor control limits specified in AEC Method E128.0, 0.95 and 1.05, should be relaxed for normal operations.

Method Blanks

The distribution of the method blank data and the variance of method blank determination are shown in Figures 7 and 8. The Shapiro Wilk W and the χ^2 goodness of fit test probabilities indicate that, unlike the calibration factor data, the method blank data do not conform to a normal distribution, a log normal distribution, or a γ distribution. This is not surprising as the method blank is the one QC test influenced by factors beyond the control of the laboratory. Sources of contamination such as laboratory reagents,

GAC, and polycarbonate filters are tested to meet method specifications; rigorous glassware preparation procedures are specified; but the contamination through building services, such as the air recirculation system and laboratory water are not completely in control of the laboratory. It is these services which cause nonrandom changes in the method blank.

The variance of the daily measurements of the blank conforms to a χ^2 type distribution, indicating that the daily estimate of the blank is a normal random variable. The variance of the daily measurement of the blank, however, is independent of the true daily blank, itself a random variable, as is illustrated in Figure 9, a scatter plot of the data ranks of the blank and the blank variance data sets. They appear to be entirely independent. This is supported by the Spearman rank correlation of -0.128 for the two data sets which does not differ significantly from zero (probability $\geq$ 0.167).

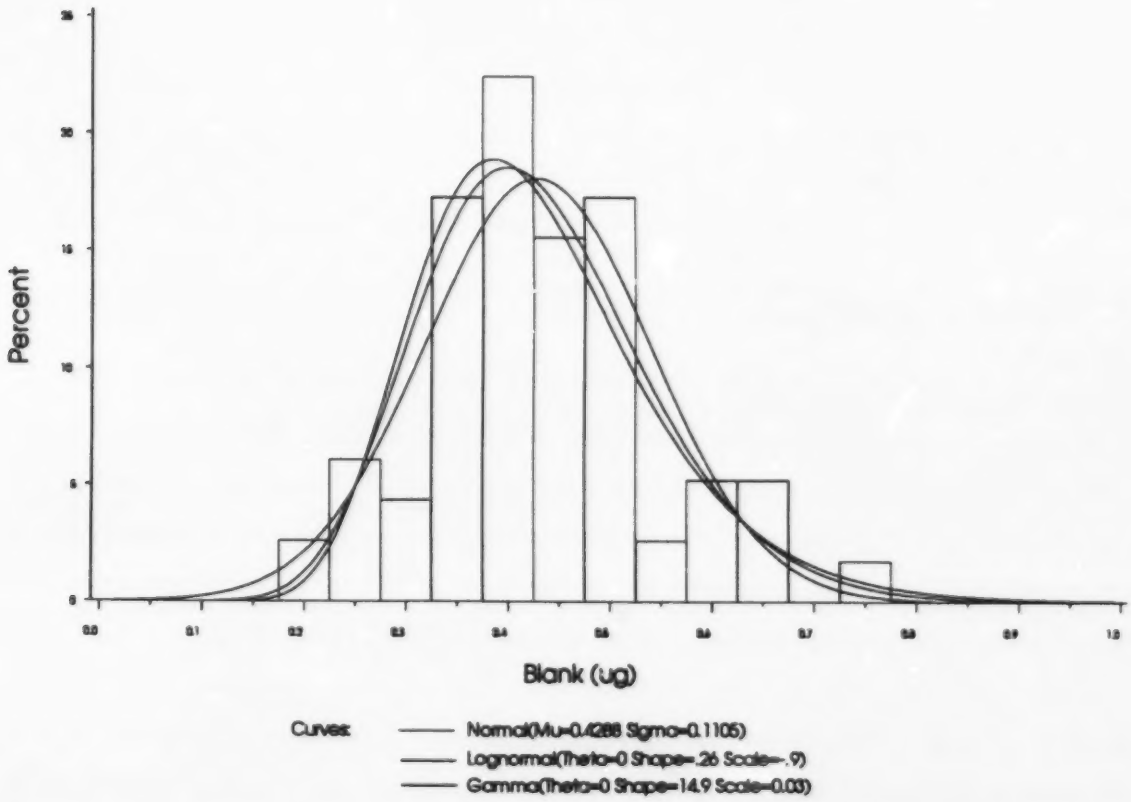

Figure 7 Distribution of method blanks and fitted normal, lognormal and γ distributions.

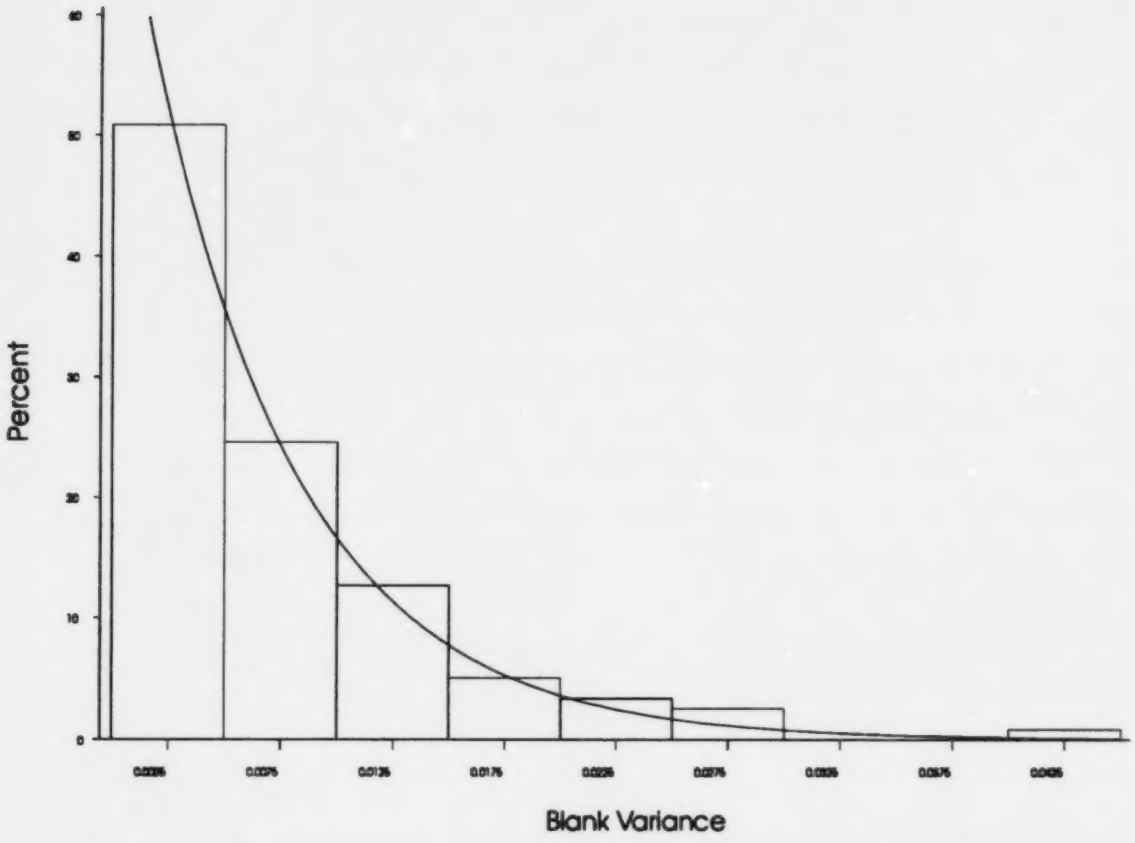

Figure 8 Distribution of method blank measurement variation and fitted χ^2 type distribution (2 degrees of freedom).

This independence of the two data sets is very important because it demonstrates that the variance in the blank measurement is not influenced by the factors affecting blank value. This means that although method performance is affected by the variance of the measurement of method blank, the effect of the method blank itself is negligible with in the range encountered. Rigorous control of the method blank is not necessary and control limits may be relaxed. Improvements in the source laboratory water used have now been made and these may be reflected in the distribution of future QC data.

Estimation of Method Variance and Method Standard Deviation

The results of the duplicate analysis of samples are used to estimate the variance and standard deviation of the method. In this discussion the only results of samples which responded in the low range of the

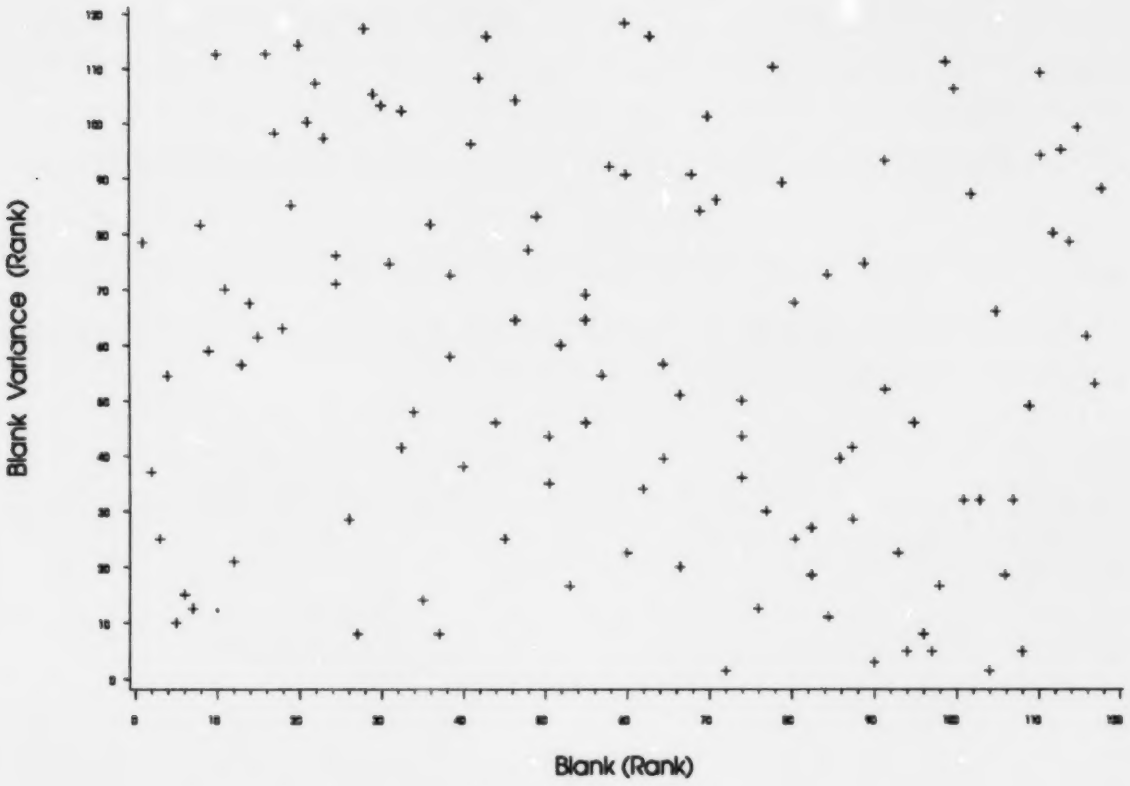

Figure 9 Scatter plot of rank of blank variance versus rank of blank.

organic halide analyzer (< 5 µg as chloride) are considered as the standard deviation at low concentrations is used to calculate the MDL. The results of duplicate analysis of more concentrated samples have also been analyzed (Table 2) and the relative differences are less than those found in low concentration samples

The variance is estimated from the square of the differences of duplicate analysis using the equation:

$$s^2 = 2 \times \left(\frac{\Delta AOX}{2}\right)^2 = \frac{\Delta AOX^2}{2} \qquad (4)$$

which was obtained by substituting ΔAOX, the difference in the instrument responses of the two analyses, into the equation for the standard deviation of a normally distributed set of data. Figure 10 shows the distribution of the square of the differences in duplicate analysis of low response samples. These data

conform to a χ^2 type distribution, the probability of a greater χ^2 value being 0.399, thus indicating a satisfactory fit of the parameters in Table 2, to the data.

The estimate of AOX method variance of the method is mean of the square of the duplicate differences divided by 2. The method standard deviation can be estimated as the square root of this estimate of the method variance, $(0.0586/2)^{0.5} = 0.17$ µg halide as chloride. This estimates the method standard deviation in terms of chloride detected. Division 0.1 L converts the method standard deviation to concentration for undiluted low concentration samples, 1.7 µg/L or 0.0017 mg/L.

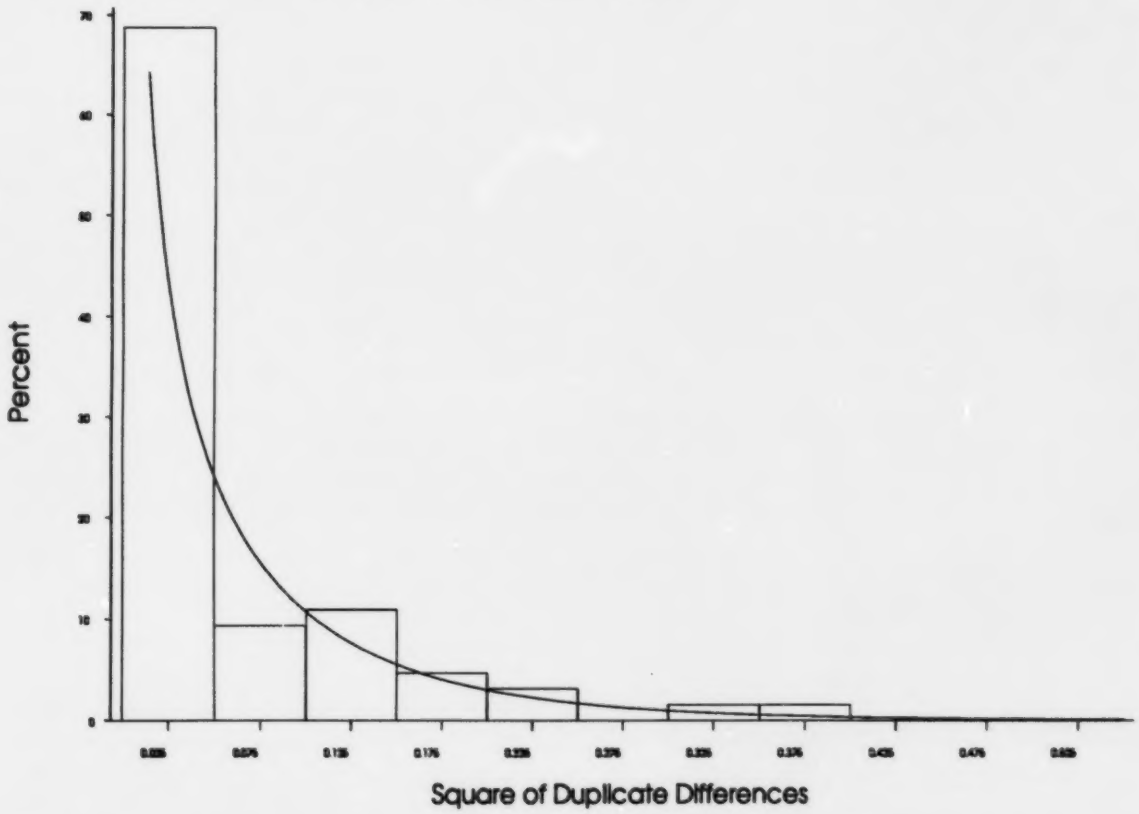

Figure 10 Distribution of squares of duplicate differences (low range) and fitted χ^2 type distribution (1 degree of freedom).

The method standard deviation for low concentration samples can also be estimated from the set of results from repeated analysis of low concentration samples. Two such sets of results are listed in Table 3. The

two estimates of the method standard deviation, 0.0013 and 0.0017 mg/L, do not differ significantly($p > 0.25$), nor do they differ significantly ($p > 0.25$) from the method standard deviation estimated from the differences in duplicate analysis. The distribution of the square of the differences also indicates that the standard deviation remains constant over time and that these estimates of method standard deviation apply to all data generated in our laboratory with this method in control. The MDL of this method in our laboratory is 0.005 mg/L and is applicable to undiluted Alberta river water receiving treated BKME.

Table 3 Results of replicate analysis of low concentration river samples.

Determination	Site #1 µg Cl	Site #2 µg Cl
1	0.0266	0.0049
2	0.0269	0.0079
3	0.0253	0.0085
4	0.0258	0.0048
5	0.0255	0.0078
6	0.0238	0.0072
7	0.0280	0.0061
8	0.0267	0.0038
9		0.0052
Average	0.0261	0.0062
Standard Deviation	0.0013	0.0017

It is inappropriate to apply this estimate of the MDL to BKME. In BKME the concentration of organic material and AOX is far higher than that found in river waters. Dilution of the sample is necessary to avoid saturation of the GAC, and/or overloading the instrument with chloride. The MDL, or standard deviation of the method, must be adjusted to take into account the dilution used. In samples with high concentrations of organic material and low concentrations of AOX, such as chemi-thermomechanical pulp (CTMP) mill effluents, the dilutions required to avoid the saturation of the GAC may make it impossible to observe any AOX.

The detection and measurement of AOX by this method is also affected by the criteria for the agreement, within 10%, of replicate analyses. In river samples, with AOX concentrations below 0.020 µg/L, the replicate criteria is difficult of fulfill although the GAC does not become saturated. The replicate criteria

is based on a relative difference which can exceed the absolute method error at these low concentrations. In such samples the replicate criteria may lead to the rejection of useful data.

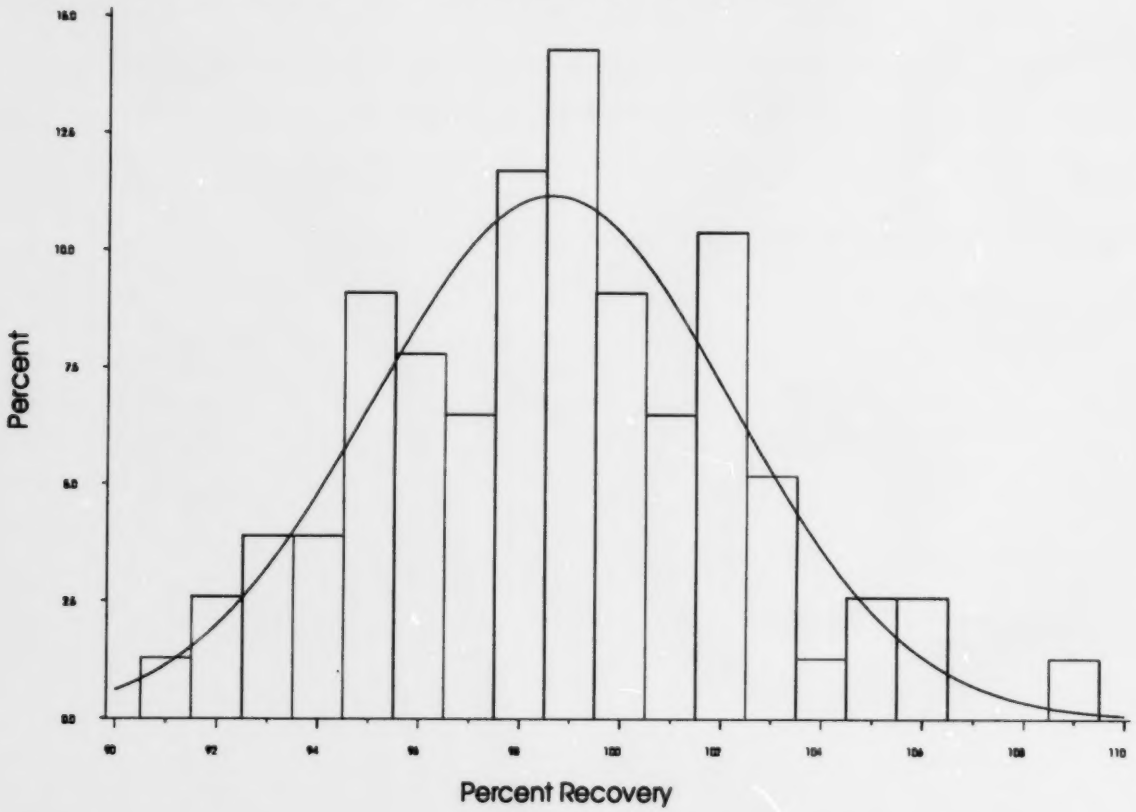

Figure 11 Distribution of the recovery of 2-chlorobenzoic acid from fortified samples and fitted normal distribution.

Recovery of 2-Chlorobenzoic Acid

The distribution of 2-chlorobenzoic acid recoveries is shown in Figure 11. This test is based on the recovery of 10 µg chloride added, as 2-chlorobenzoic acid, to samples. The recovery will be influenced by: systematic errors due to calibration; a high variation in the blank; or poor sample adsorption.

The data are normally distributed with probabilities of 0.925 for a greater Shapiro Wilk W test statistic and 0.647 for the χ^2 goodness of fit test of the fitted distribution (Table 2). The mean recovery of 98.62%

indicates almost quantitative recovery of the spiked acid. The standard deviation of 3.57% indicates an approximate standard deviation of 0.36 µg (based on a 10 µg determination) which is considerably higher than the estimates of the method standard deviation in the preceding section. This is due to a number of factors: method results are based on the average of two replicate analysis, not one determination as with the spiked sample; the recovery is calculated using the difference of analyses, which increases the random error; the recovery contains random error associated with the addition of the 2-chlorobenzoic acid to the sample; and the instrument range used in the analysis of the spiked sample is > 10 µg where the absolute error is higher than the error in the low concentration data used above to estimate the method standard deviation.

The recovery then is not a particularly sensitive QC test but, as failures in this test should be accompanied by the failure of another QC test, it can be used to confirm other test failures, to discriminate between random events or real changes in the test. It may also be used to determine if the GAC is saturated in the analysis of low AOX concentration where the replicate criteria is not met.

QCA/QCB Calibration Check Standards

The QCA/QCB test is used to evaluate the instrument calibration. Two measurements of standard solutions, one at 70% of the instrument range (QCA), and one at 20% of the instrument range (QCB) are made. The measurements are corrected for calibration and the sum and difference are used to evaluate the slope and intercept of the calibration respectively (note in this method the zero is always used as the intercept). The analysis and discussion of this test data presented here is only preliminary as the data set contains only 33 points. The distributions of the sum and difference data sets, along with the probabilities of the Shapiro Wilk W test and the χ^2 test of fit, are listed in Table 2.

The test results in Table 2 indicate that the distribution of the sum data is normal but that the difference of the difference data differs significantly from normality. However, as this discussion is preliminary and involves a small data set, the difference data will be treated as normally distributed to simplify the analysis.

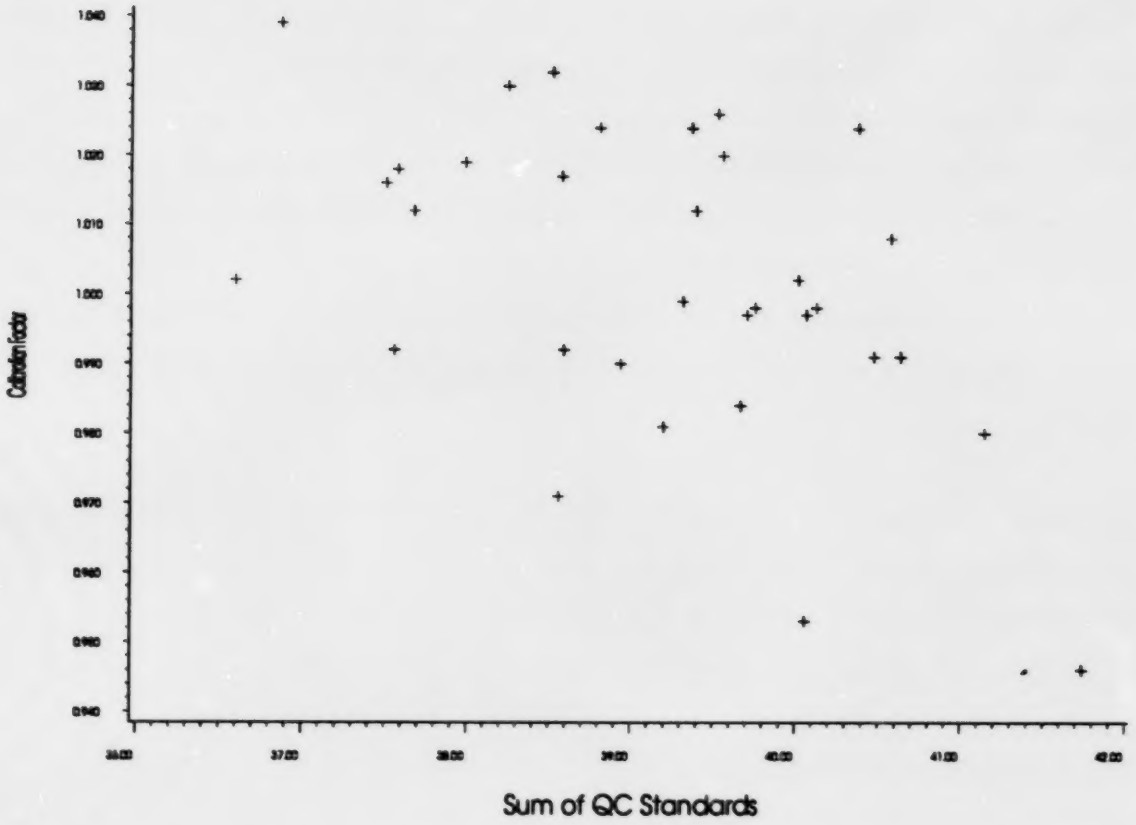

Figure 12 Scatter plot of calibration factor and QCA/QCB sum parameter.

The standard deviation of the sum data is 1.23 µg chloride, which although not unreasonable as it contains the errors of a mid range (5 to 15 µg chloride) and a high range measurement (greater than 15 µg chloride), suggests that this test may not be precise enough for tight control of the calibration factor. Figure 12 shows the scatter plot of the calibration factor versus the sum data. A negative correlation between the two sets of data is obvious. The Pearson correlation of -0.487 between the sets of data is significantly different from 0 at $P \leq 0.004$. It is apparent the that this test is sensitive to errors in the estimation of the calibration factor although a simple Shewart chart of the data may not be an effective method to analyze the daily results. Analysis using a scatter plot, or a Shewart chart of a function of the calibration factor and the sum result, may prove to be more effective in detecting outliers. This will be investigated further as more data become available.

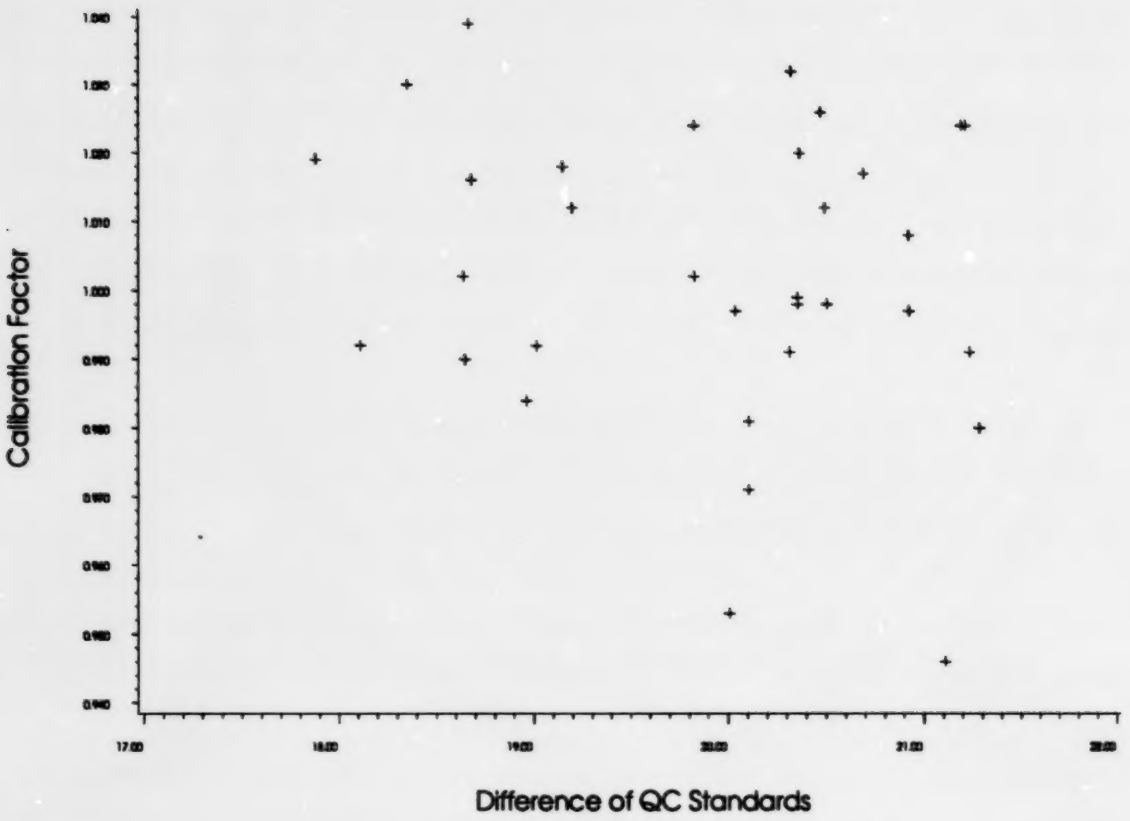

Figure 13 Scatter plot of calibration factor and QCA/QCB difference parameter.

The scatter plot of the calibration factor and the difference data is shown in Figure 13. The two data sets are not correlated; the Pearson correlation coefficient (-0.189) does not differ significantly different than zero (probability ≥ 0.293). This is not unexpected as the difference between QCA and QCB is meant to be used to control the intercept and should have a very low correlation the slope of the calibration. The standard deviation in the difference data is 1.00 µg, suggesting that it has little value in controlling the calibration intercept.

As part of the instrument operating procedure, the instrument is cycled repeatedly at startup with no sample, until the chloride is detected at less than 0.05 µg. Under normal conditions the instrument blank remains relatively constant and the calibration intercept is treated as zero. However, data will continue to be collected so that the effectiveness of the test may be analyzed more rigorously.

Conclusions

1. The method standard deviation of this analysis is approximately 0.0017 mg/L AOX as chloride for undiluted river waters receiving pulp and paper effluents and the true MDL for these samples is approximately 0.005 mg/L AOX as chloride. The method standard deviation for BKME samples is 0.0023 mg/L (based on the mid range replicate differences) adjusted for the dilution used in the analysis. This results in a method standard deviation of 0.23 mg/L for BKME samples diluted 1.0 mL to 100 mL.

2. The calibration factor and blank control limits may be relaxed with little or no impact on method performance. The variance of the measurement of these parameters, which effect method performance and are independent of the measurements, must be monitored and controlled rigorously.

3. All QC test results, with the exception of the method blank, are either normal or χ^2 type random variates, therefore the probabilities used in the calculation of control limits are true probabilities.

4. The QCA/QCB sum parameter is significantly correlated with the calibration factor and although there is considerable random error in the parameter, it may be possible to use it in conjunction with the calibration factor to effectively control the calibration factor. The QCA/QCB difference parameter appears to contain too much random error to be useful in the control of a calibration intercept.

Revision to be Made to AEC Method E128.0

1. The AEC method E128.0 will be revised to be applicable to receiving waters as well as bleached kraft mill effluents. Accordingly the method has been renamed to AE128.1 to reflect these changes.

2. The stated MDL of method E128.0 for undiluted samples will be lowered to 0.010 mg/L AOX as chloride. The replicate criteria of 10% should only be rigorously applied to samples over 0.020 mg/L AOX as chloride and when not met in less concentrated samples the results may be reported with the failure to meet the replicate criteria noted.

3. The control limits for the calibration factor and the blank should be relaxed to 0.90 to 1.05 for the calibration factor and less than 0.75 for the blank. Data generated using these relaxed limits should be analyzed for any negative impact of these changes on data quality.

4. QCA/QCB data should continue to be collected and the sum and difference parameters should be further evaluated when enough data is available.

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Appendix 1

Quality Control Data from February 1990 to May 1991

Table A1.1

Quality control data from February 1990 to May 1991.

OBS	DATE	BLANK	BK_STD	CAL_FAC	CF_STD	QCAPLUS	QCAMINUS	BK_VAR	CF_VAR
1	15MAR1991	0.582	0.003	0.980	0.001	41.15	21.29	0.000009	0.000001
2	13SEP1990	0.452	0.003	0.989	0.005	38.98	22.67	0.000009	0.000025
3	25MAY1990	0.489	0.004	0.983	0.001	37.31	21.88	0.000016	0.000001
4	21JUN1990	0.616	0.009	1.008	0.001	36.09	20.83	0.000081	0.000001
5	08MAR1991	0.506	0.009	1.020	0.002	39.56	20.37	0.000081	0.000004
6	26MAR1991	0.499	0.009	1.008	0.003	40.58	20.93	0.000081	0.000009
7	06NOV1990	0.377	0.011	0.943	0.003	38.05	22.68	0.000121	0.000009
8	31MAY1990	0.359	0.011	0.986	0.009	36.06	19.99	0.000121	0.000081
9	17SEP1990	0.505	0.011	0.960	0.009	39.18	22.87	0.000121	0.000081
10	01FEB1991	0.241	0.012	0.946	0.012	41.74	21.11	0.000144	0.000144
11	18JAN1991	0.482	0.013	1.012	0.004	37.68	19.20	0.000169	0.000016
12	28AUG1990	0.243	0.015	1.010	0.007	37.48	21.31	0.000225	0.000049
13	02APR1990	0.457	0.015	0.975	0.017	40.28	22.84	0.000225	0.000289
14	06JUN1990	0.374	0.017	0.996	0.027	37.40	21.92	0.000289	0.000729
15	14MAR1990	0.242	0.021	0.976	0.014	37.48	22.12	0.000441	0.000196
16	21MAR1990	0.398	0.022	0.970	0.015	38.58	22.90	0.000484	0.000225
17	15FEB1991	0.518	0.022	0.984	0.019	39.67	18.97	0.000484	0.000361
18	19OCT1990	0.600	0.023	1.005	0.004	39.48	23.02	0.000529	0.000016
19	22MAR1991	0.481	0.023	1.024	0.005	40.38	21.20	0.000529	0.000025
20	04MAR1991	0.440	0.024	1.039	0.003	36.87	18.67	0.000576	0.000009
21	01JUN1990	0.296	0.025	0.977	0.001	.	.	0.000625	0.000001
22	29JAN1991	0.497	0.028	1.002	0.023	36.60	18.64	0.000784	0.000529
23	20AUG1990	0.424	0.028	0.992	0.024	37.41	21.79	0.000784	0.000576
24	16MAR1990	0.220	0.030	0.994	0.005	.	.	0.000900	0.000025
25	08JUN1990	0.387	0.030	0.985	0.009	37.85	21.15	0.000900	0.000081
26	12MAR1991	0.475	0.030	0.991	0.014	40.48	20.32	0.000900	0.000196
27	18MAR1991	0.481	0.031	1.012	0.001	39.40	20.50	0.000961	0.000001
28	30NOV1990	0.357	0.032	1.061	0.007	36.15	22.19	0.001024	0.000049
29	27FEB1991	0.486	0.032	0.992	0.010	38.59	19.02	0.001024	0.000100
30	25MAR1991	0.466	0.033	0.997	0.006	40.07	20.93	0.001089	0.000036
31	31OCT1990	0.559	0.034	0.976	0.002	41.04	23.87	0.001156	0.000004
32	16JAN1991	0.577	0.034	1.024	0.009	38.81	19.83	0.001156	0.000081
33	21FEB1991	0.615	0.034	0.990	0.032	38.94	18.65	0.001156	0.001024
34	20MAR1990	0.435	0.035	0.952	0.003	40.57	25.20	0.001225	0.000009
35	30AUG1990	0.392	0.036	0.975	0.006	38.13	22.22	0.001296	0.000036
36	19MAR1991	0.453	0.037	1.017	0.004	38.58	20.70	0.001369	0.000016
37	16FEB1990	0.210	0.038	0.965	0.004	41.10	24.35	0.001444	0.000016
38	11DEC1990	0.380	0.039	1.032	0.005	38.84	22.95	0.001521	0.000025
39	06MAR1991	0.483	0.040	0.999	0.001	39.32	20.36	0.001600	0.000001
40	29NOV1990	0.438	0.040	1.001	0.008	39.08	23.70	0.001600	0.000064
41	02MAY1990	0.367	0.043	0.946	0.002	38.54	22.39	0.001849	0.000004
42	21MAR1991	0.486	0.043	0.971	0.005	38.56	20.11	0.001849	0.000025
43	20MAR1991	0.453	0.045	0.991	0.010	40.64	21.24	0.002025	0.000100
44	14SEP1990	0.392	0.045	0.967	0.025	37.57	22.40	0.002025	0.000625
45	01MAR1990	0.386	0.046	0.969	0.009	.	.	0.002116	0.000081
46	14MAR1991	0.502	0.046	0.998	0.017	39.76	20.36	0.002116	0.000289
47	13FEB1990	0.402	0.046	0.994	0.030	.	.	0.002116	0.000900
48	11JUN1990	0.373	0.047	0.988	0.011	38.37	23.03	0.002209	0.000121
49	12FEB1991	0.625	0.048	0.953	0.004	40.06	20.01	0.002304	0.000016
50	25FEB1991	0.453	0.050	1.030	0.002	38.25	18.35	0.002500	0.000004
51	26MAR1990	0.440	0.053	0.970	0.015	37.26	22.71	0.002809	0.000225
52	17JAN1991	0.495	0.054	1.032	0.006	38.52	20.33	0.002916	0.000036
53	18JUN1990	0.857	0.056	0.963	0.013	38.56	22.73	0.003136	0.000169
54	06DEC1990	0.235	0.063	1.060	0.004	34.77	18.88	0.003969	0.000016
55	27MAR1990	0.403	0.063	0.975	0.021	35.71	20.80	0.003969	0.000441
56	04SEP1990	0.438	0.065	1.014	0.004	37.12	20.84	0.004225	0.000016
57	25JUL1990	0.314	0.065	0.986	0.015	36.50	22.27	0.004225	0.000225
58	01MAY1990	0.379	0.066	1.000	0.002	39.13	23.24	0.004356	0.000004
59	28MAY1990	0.267	0.069	0.982	0.002	36.98	23.63	0.004761	0.000004
60	31AUG1990	0.394	0.070	1.037	0.006	36.45	20.75	0.004900	0.000036
61	15JAN1991	0.755	0.071	1.024	0.001	39.37	21.22	0.005041	0.000001
62	07DEC1990	0.322	0.071	1.016	0.011	40.18	23.72	0.005041	0.000121
63	14NOV1990	0.328	0.072	1.002	0.014	36.64	22.49	0.005184	0.000196
64	21AUG1990	0.388	0.073	0.999	0.006	37.35	21.63	0.005329	0.000036
65	05SEP1990	0.402	0.073	1.005	0.013	38.25	21.92	0.005329	0.000169
66	14JAN1991	0.587	0.074	1.026	0.008	39.53	20.48	0.005476	0.000064
67	10DEC1990	0.475	0.075	1.030	0.003	40.23	23.90	0.005625	0.000009
68	15MAR1990	0.320	0.075	0.966	0.021	37.23	21.94	0.005625	0.000441
69	09MAR1990	0.402	0.076	0.972	0.003	37.87	20.71	0.005776	0.000009
70	10MAY1990	0.277	0.077	1.028	0.024	35.61	20.55	0.005929	0.000576
71	06APR1990	0.355	0.079	1.001	0.021	36.65	21.75	0.006241	0.000441
72	27MAR1991	0.482	0.081	0.998	0.004	40.13	20.51	0.006561	0.000016
73	12MAR1990	0.379	0.081	0.988	0.005	36.20	21.48	0.006561	0.000025
74	30MAR1990	0.366	0.083	1.024	0.018	37.24	21.65	0.006889	0.000324

Table A1.1 (continued)

Quality control data from February 1990 to May 1991.

OBS	DATE	BLANK	BK_STD	CAL_FAC	CF_STD	QCAPLUS	QCAMINUS	BK_VAR	CF_VAR
75	11SEP1990	0.488	0.083	0.973	0.025	39.63	23.52	0.006889	0.000625
76	20JUL1990	0.355	0.084	1.019	0.014	38.13	21.87	0.007056	0.000196
77	05MAR1990	0.390	0.085	0.979	0.011	37.41	21.20	0.007225	0.000121
78	07MAR1990	0.191	0.086	0.977	0.019	37.02	21.18	0.007396	0.000361
79	21JAN1991	0.658	0.086	1.018	0.025	37.58	19.15	0.007396	0.000625
80	18JUL1990	0.647	0.087	1.008	0.015	38.20	21.53	0.007569	0.000225
81	27JUL1990	0.250	0.089	0.983	0.001	38.16	22.67	0.007921	0.000001
82	13MAR1990	0.376	0.089	0.946	0.007	37.38	20.94	0.007921	0.000049
83	28FEB1991	0.391	0.090	1.002	0.018	40.02	19.83	0.008100	0.000324
84	22OCT1990	0.447	0.091	1.009	0.003	39.76	24.12	0.008281	0.000009
85	29MAR1990	0.330	0.093	0.981	0.001	.	.	0.008649	0.000001
86	20FEB1991	0.451	0.094	0.992	0.016	37.56	18.11	0.008836	0.000256
87	24AUG1990	0.570	0.097	1.014	0.021	37.14	21.25	0.009409	0.000441
88	15JUN1990	0.993	0.098	0.975	0.013	37.16	20.91	0.009604	0.000169
89	16OCT1990	0.471	0.099	1.020	0.011	36.27	19.40	0.009801	0.000121
90	19SEP1990	0.424	0.100	1.023	0.005	36.09	20.64	0.010000	0.000025
91	27AUG1990	0.442	0.100	1.019	0.007	37.50	21.32	0.010000	0.000049
92	20FEB1990	0.404	0.102	0.987	0.002	40.18	22.10	0.010404	0.000004
93	26FEB1991	0.495	0.103	1.019	0.033	37.99	17.88	0.010609	0.001089
94	25JUN1990	0.644	0.104	1.000	0.022	36.80	21.49	0.010816	0.000484
95	12SEP1990	0.649	0.106	0.980	0.038	39.39	22.20	0.011236	0.001444
96	03MAY1990	0.381	0.107	0.973	0.001	36.74	20.84	0.011449	0.000001
97	02MAR1990	0.351	0.109	0.970	0.004	37.41	22.57	0.011881	0.000016
98	08MAR1990	0.326	0.111	0.990	0.003	36.56	21.29	0.012321	0.000009
99	14AUG1990	0.737	0.112	0.984	0.011	37.99	21.72	0.012544	0.000121
100	17AUG1990	0.344	0.114	0.982	0.009	38.53	21.88	0.012996	0.000081
101	28MAR1990	0.450	0.115	0.957	0.010	38.03	20.13	0.013225	0.000100
102	03APR1990	0.367	0.116	1.046	0.015	35.09	20.71	0.013456	0.000225
103	18OCT1990	0.365	0.120	0.979	0.027	39.51	23.27	0.014400	0.000729
104	19MAR1990	0.388	0.122	0.963	0.002	38.81	20.53	0.014884	0.000004
105	22MAR1990	0.364	0.124	0.969	0.003	36.23	21.02	0.015376	0.000009
106	14FEB199'	0.550	0.125	1.016	0.000	37.51	18.68	0.015625	0.000010
107	01NOV1990	0.348	0.126	0.962	0.009	37.69	21.71	0.015876	0.000081
108	06MAR1990	0.383	0.131	0.951	0.014	38.02	20.77	0.017161	0.000196
109	17OCT1990	0.644	0.134	0.959	0.007	40.68	25.15	0.017956	0.000049
110	05MAR1991	0.470	0.139	0.997	0.020	39.71	20.04	0.019321	0.000400
111	07MAR1991	0.522	0.143	0.981	0.002	39.20	20.11	0.020449	0.000004
112	22JUN1990	0.325	0.145	0.963	0.011	39.11	21.77	0.021025	0.000121
113	08MAY1990	0.269	0.145	0.991	0.014	37.02	21.18	0.021025	0.000196
114	04APR1990	0.337	0.146	1.008	0.012	37.27	21.08	0.021316	0.000144
115	24JUL1990	0.437	0.159	1.022	0.002	38.50	22.06	0.025281	0.000004
116	12JUN1990	0.385	0.159	0.958	0.014	.	.	0.025281	0.000196
117	09APR1990	0.362	0.172	0.960	0.009	38.16	23.05	0.029584	0.000081
118	29AUG1990	0.424	0.200	0.999	0.013	36.99	21.01	0.040000	0.000169

Table A1.2

LOW RANGE DUPLICATE DATA

	SAMPLE	MATRIX	DIFFERENCE	SQUARE		SAMPLE	MATRIX	DIFFERENCE	SQUARE
1	TB-FTMC	TB	0.144	0.020740	35	T034-1143	SW	0.302	0.091200
2	T007-0176	EF	0.091	0.008280	36	T034-1159	SW	0.069	0.004760
3	T007-0177	EF	0.002	0.000000	37	T034-1129	SW	0.039	0.001520
4	T008-0217	SW	0.195	0.038030	38	T037-1186	SW	0.117	0.013690
5	T008-0215	EF	0.045	0.002020	39	T037-1223	TW	0.378	0.142880
6	T009-0238	SW	0.123	0.015130	40		SW	0.001	0.000000
7	T009-0256	EF	0.083	0.006890	41	T042-1301	SW	0.967	0.935090
8	T010-0282	SW	0.069	0.004760	42		SW	0.001	0.000000
9	T010-0283	SW	0.010	0.000100	43	T044-1384	SW	0.240	0.057600
10	T010-0286	SW	0.330	0.108900	44	T044-1386	SW	0.826	0.682280
11	T010-0300	SW	0.001	0.000000	45	T045-1439	SW	0.232	0.053820
12	T010-0301	EF	0.210	0.044100	46	T047-1469	TW	0.366	0.133960
13	T010-0304	SW	0.182	0.033120	47	T047-1498	TW	0.156	0.024340
14	T010-0317	EF	0.098	0.009600	48	T049-1600	SW	0.110	0.012100
15	T010-0320	SW	0.122	0.014880	49	T049-1632	TW	0.336	0.112900
16	T010-0285	SW	0.073	0.005330	50	QC SMP-00	TW	0.132	0.017420
17	T010-0287	SW	0.011	0.000120	51	T102-0073	TW	0.407	0.165650
18	T011-0354	EF	0.169	0.028560	52	T104-0089	SW	0.078	0.006080
19	T011-0356	SW	0.442	0.195360	53	T105-0092	SW	0.472	0.222780
20	T011-0360	SW	0.020	0.000400	54	T106-0120	SW	0.183	0.033490
21	T012-0415	TW	0.060	0.003600	55	T107-0136	SW	0.048	0.002300
22	LB-SMP-MA	SL	0.246	0.060520	56	T107-0162	SW	0.766	0.586760
23	INT-LEA-1	EF	0.079	0.006240	57	T108-0255	SW	0.090	0.008100
24	T013-0462	SW	0.337	0.113570	58	T108-0259	SW	0.916	0.839060
25	T018-0574	SW	0.041	0.001680	59	T108-0262	SW	0.391	0.152880
26	T021-0617	SW	0.043	0.001850	60	T109-0339	SW	0.614	0.377000
27	T022-0675	TW	0.028	0.000780	61	T111-0428	SW	0.084	0.007060
28	T025-0849	TW	0.007	0.000050	62	T111-0426	SW	0.356	0.126740
29	T030-0993	SW	0.163	0.026570	63	T111-0561	SW	0.164	0.026900
30	T030-1001	SW	0.289	0.083520	64	T112-0574	SW	0.559	0.312480
31	T033-1086	SW	0.163	0.026570	65	T110-0418	SW	0.364	0.132500
32	T033-1099	SW	0.143	0.020450	66	T113-0626	SW	0.251	0.063000
33	T034-1142	SW	0.495	0.245020	67	T116-0713	SW	0.121	0.014640
34	T034-1144	SW	0.001	0.000000	68	T113-0626	SW	0.051	0.002600

Table A1.3

MID RANGE DUPLICATE DATA

	SAMPLE	MATRIX	DIFFERENCE	SQUARE		SAMPLE	MATRIX	DIFFERENCE	SQUARE
1	T007-0106	EF	0.153	0.023410	18	T034-1133	EF	0.979	0.958440
2	T007-0179	SW	0.001	0.000000	19	T034-1145	SW	0.212	0.044940
3	T008-0194	SW	0.001	0.000000	20	T049-1603	TW	0.363	0.131770
4	T009-0253	SW	0.607	0.368450	21	T049-1601	TW	0.112	0.012540
5	T010-0302	SW	0.425	0.180620	22	T102-0006	SW	0.443	0.196250
6	INT-LEACH	LE	0.268	0.071820	23	T102-0014	SW	0.615	0.378220
7	T013-0451	SW	0.553	0.305810	24	T102-0016	SW	0.120	0.014400
8	T017-0557	TW	0.105	0.011020	25	T107-0138	SW	0.518	0.268320
9	T019-0579	EF	0.105	0.011020	26	T107-0199	SW	0.172	0.029580
10	T021-0647	TW	1.861	3.463320	27	T107-0203	SW	0.205	0.042020
11	T022-0684	EF	1.130	1.276900	28	T108-0263	SW	0.074	0.005480
12	T023-0730	EF	0.300	0.090000	29	T108-0282	SW	0.053	0.002810
13	T023-0733	EF	0.163	0.026570	30	T110-0390	SW	0.234	0.054760
14	T023-0736	EF	0.105	0.011020	31	T111-0385	EF	0.085	0.007230
15	T028-0928	EF	0.025	0.000630	32	T112-0611	SW	0.484	0.234260
16	T028-0929	EF	0.605	0.366020	33	T112-0613	SW	0.472	0.222780
17	T033-1083	TW	0.393	0.154450					

Table A1.4

2-Chlorobenzoic Acid Recovery

OBS	SAMPLE	MATRIX	RESULT	RECOVERY	OBS	SAMPLE	MATRIX	RESULT	RECOVERY
1	T007-0174	SW	0.010	98.0	41	T042-1334	SW	0.010	99.3
2	T007-0179	SW	0.090	100.4	42	T044-1384	SW	0.012	105.5
3	T008-0195	SW	0.080	94.8	43	T044-1386	SW	0.000	102.1
4	T008-0194	SW	0.070	94.1	44	T045-1439	SW	0.014	100.3
5	T008-0216	SW	0.040	96.0	45	T049-1600	SW	0.035	91.6
6	T009-0238	SW	0.000	94.9	46	T102-0006	SW	0.305	94.8
7	T010-0282	SW	0.000	93.4	47	T102-0010	SW	0.004	94.4
8	T010-0286	SW	0.040	98.6	48	T102-0014	SW	0.059	95.4
9	T010-0300	SW	0.030	98.8	49	T102-0016	SW	0.069	92.9
10	T010-0304	SW	0.410	98.7	50	T104-0089	SW	0.044	97.4
11	T010-0320	SW	0.260	97.0	51	T105-0092	SW	0.013	98.1
12	T010-0302	SW	0.355	100.9	52	T106-0120	SW	0.001	94.8
13	T011-0330	SW	0.002	96.5	53	T107-0136	SW	-0.003	102.7
14	T011-0353	SW	0.006	102.4	54	T107-0162	SW	0.003	102.0
15	T011-0355	SW	0.022	98.6	55	T107-0187	SW	0.150	108.7
16	T011-0360	SW	0.019	103.9	56	T107-0199	SW	0.077	101.7
17	T012-0402	SW	0.020	100.3	57	T107-0203	SW	0.124	98.1
18	T013-0428	SW	0.013	98.1	58	T108-0255	SW	0.009	98.1
19	T013-0462	SW	0.013	94.1	59	T108-0259	SW	0.006	105.7
20	T013-0464	SW	0.030	100.9	60	T108-0262	SW	0.007	98.9
21	T025-0828	SW	0.013	97.8	61	T108-0263	SW	0.239	98.6
22	T025-0850	SW	0.006	95.9	62	T108-0282	SW	0.092	99.5
23	T029-0982	SW	0.087	100.2	63	T109-0308	SW	0.001	99.8
24	T030-0993	SW	0.001	100.8	64	T109-0339	SW	0.006	103.3
25	T030-1001	SW	0.018	96.2	65	T110-0390	SW	0.074	102.3
26	T033-1086	SW	0.012	100.7	66	T111-0428	SW	0.050	98.5
27	T033-1099	SW	0.002	99.8	67	T111-0426	SW	0.036	104.7
28	T034-1142	SW	0.030	98.4	68	T111-0561	SW	0.021	101.7
29	T034-1144	SW	0.027	88.1	69	T112-0574	SW	0.045	95.9
30	T034-1132	SW	-0.003	102.6	70	T112-0588	SW	0.042	98.1
31	T034-1143	SW	0.027	94.6	71	T110-0418	SW	0.375	101.9
32	T034-1145	SW	0.053	88.6	72	T112-0611	SW	0.145	97.3
33	T034-1159	SW	0.014	99.0	73	T112-0613	SW	0.658	94.7
34	T034-1129	SW	0.001	90.6	74	T113-0626	SW	0.053	101.5
35	MDL-DUP 2	SW	0.026	116.3	75	T112-0629	SW	0.015	98.5
36	T037-1185	SW	0.012	97.5	76	T116-0713	SW	-0.001	102.6
37	T037-1186	SW	0.012	95.8	77	T112-0613	SW	0.578	98.8
38	T037-1184	SW	0.008	92.9	78	T113-0626	SW	0.045	96.0
39	T041-1287	SW	0.042	96.8	79	T118-0792	SW	0.478	100.8
40	T042-1301	SW	0.006	91.9	80	T118-0796	SW	0.191	104.8

Appendix 2

SAS Source Code for the Statistical Analysis of Quality Control Data

```
GOPTIONS DEV=HP7475A GSFNAME=OUT GSFMODE=REPLACE
COLORS=(BLACK BLACK BLACK BLACK BLACK BLACK BLACK BLACK);

**********  CALIBRATION FACTOR  **********;

FILENAME OUT 'CIJ0101.HPG';
PROC CAPABILITY DATA = I.NEWDATA   GRAPHICS  NORMAL;
                VAR CAL_FAC ;
                LABLE CAL_FAC ='Calibration Factor';
                HISTOGRAM
                     /   NOLEGEND
                         NORMAL
                         MIDPOINTS=0.90 TO 1.10 BY 0.010 ;
RUN;

***********  CALIBRATION FACTOR VARIANCE  ***********;

FILENAME OUT 'CIJ0102.HPG';
PROC CAPABILITY DATA = I.NEWDATA   GRAPHICS   NORMAL ;
                VAR CF_VAR ;
                LABLE  CF_VAR  =  'Calibration  Factor  Measurement
Variance';
                HISTOGRAM
                   /    NOLEGEND
                        GAMMA( ALPHA=0.5)
                        MIDPOINTS = 0.0 TO 0.0015 BY 0.0001;
RUN;

***********  METHOD BLANK  **********;

FILENAME OUT 'CIJ0104.HPG';
PROC CAPABILITY DATA = I.NEWDATA   GRAPHICS   NORMAL ;
                WHERE BLANK < 0.8;
                VAR BLANK       ;
                LABEL BLANK = 'Blank (ug)';
                HISTOGRAM
                     / NORMAL
                       LOGNORMAL
                       GAMMA
                       MIDPOINTS = 0 TO 1.0 BY .05 ;
RUN;

**********  BLANK VARIANCE  **********;

FILENAME OUT 'CIJ0105.HPG';
PROC CAPABILITY DATA = I.NEWDATA   GRAPHICS   NORMAL ;
                VAR BK_VAR       ;
                LABEL BK_VAR = 'Blank Variance' ;
                HISTOGRAM
                     /  NOLEGEND
                        GAMMA( ALPHA=1);
RUN;
```

```
**********  LOW RANGE DUPLICATES  **********;

FILENAME OUT 'CIJ0107.HPG';
PROC CAPABILITY DATA = I.DUPDATA   GRAPHICS;
                WHERE SQUARE < 0.5;
                VAR SQUARE ;
                LABEL SQUARE = 'Duplicate Differences Squared' ;
                HISTOGRAM
                     /  NOLEGEND
                        GAMMA ( ALPHA=0.5 )
                        MIDPOINTS= 0.025 TO 0.525 BY 0.05 ;
RUN;

**********  MID RANGE DUPLICATES  **********;

FILENAME OUT 'CIJ0006.HPG';
PROC CAPABILITY DATA = I.DUPMID  GRAPHICS;
                WHERE SQUARE < 0.9;
                VAR SQUARE ;
                LABEL SQUARE = 'Duplicate Differences Squared' ;
                HISTOGRAM
                     /   NOLEGEND
                         GAMMA  (ALPHA=0.5)
                         MIDPOINTS= 0.0 TO 1.0 BY 0.05;
RUN;

**********  2-CHLOROBENZOIC ACID RECOVERY  **********;

FILENAME OUT 'CIJ0108.HPG';
PROC CAPABILITY DATA = I.RECVDATA   GRAPHICS   NORMAL ;
                WHERE RECOVERY > 90 AND RECOVERY < 110;
                VAR RECOVERY       ;
                LABEL RECOVERY = 'Percent Recovery';
                HISTOGRAM
                     /   NOLEGEND
                         NORMAL
                         MIDPOINTS= 90 TO 110 BY 1;
RUN;

**********      QUALITY   CONTROL   STANDADARDS   VRS   CALIBRATION
**********;

DATA TWO;
     SET I.NEWDATA;
     WHERE DATE > '01JAN91'D;
RUN;

FILENAME OUT 'CIJ0109.HPG';
PROC GPLOT DATA=TWO;
           PLOT CAL_FAC * QCAPLUS;
RUN;

FILENAME OUT 'CIJ0110.HPG';
PROC GPLOT DATA=TWO;
           PLOT CAL_FAC * QCAMINUS;
RUN;
```

```
PROC CORR DATA=TWO PEARSON ;
          VAR CAL_FAC QCAPLUS QCAMINUS;
RUN;

**********  CORRELATION OF VARIATION AND MEASURMENT **********;

PROC CORR DATA=I.NEWDATA SPEARMAN ;
          VAR CAL_FAC CF_VAR;
RUN;

PROC CORR DATA=I.NEWDATA SPEARMAN ;
          VAR BLANK BK_VAR;
RUN;

PROC CORR DATA=I.NEWDATA SPEARMAN ;
          VAR CAL_FAC CF_VAR;
RUN;

PROC CORR DATA=I.NEWDATA SPEARMAN ;
          VAR BLANK BK_VAR;
RUN;

PROC CAPABILITY DATA=TWO NORMAL GRAPHICS ;
                VAR QCAPLUS;
                HISTOGRAM /NORMAL ;
RUN;

PROC CAPABILITY DATA=TWO NORMAL GRAPHICS ;
                VAR QCAMINUS;
                HISTOGRAM /NORMAL ;
RUN;

PROC RANK  DATA=I.NEWDATA OUT=RANKDATA ;
           VAR CAL_FAC  CF_VAR  BLANK  BK_VAR;
           RANKS CF_RANK CFV_RANK BK_RANK BKV_RANK;
RUN;

FILENAME OUT 'CIJ0103.HPG';
PROC GPLOT DATA=RANKDATA;
           LABEL CFV_RANK = 'Rank of Calibration Factor Variance'
                  CF_RANK = 'Rank of Calibration Factor';
           PLOT CFV_RANK * CF_RANK;
RUN;

FILENAME OUT 'CIJ0106.HPG';
PROC GPLOT DATA=RANKDATA;
           LABEL BKV_RANK = 'Rank of Blank Variance'
                  BK_RANK = 'Rank of Blank';
           PLOT BKV_RANK * BK_RANK;
RUN;
```

Appendix 3

SAS® Reports

CAPABILITY

Variable=CAL_FAC Calibration Factor

Moments

N	118	Sum Wgts	118
Mean	0.992856	Sum	117.157
Std Dev	0.025157	Variance	0.000633
Skewness	0.262153	Kurtosis	-0.30599
USS	116.3941	CSS	0.074049
CV	2.53384	Std Mean	0.002316
T:Mean=0	428.7083	Prob>|T|	0.0000
Sgn Rank	3510.5	Prob>|S|	0.0000
Num ^= 0	118		
W:Normal	0.974054	Prob<W	0.205

Quantiles(Def=5)

100% Max	1.061	99%	1.06
75% Q3	1.012	95%	1.032
50% Med	0.991	90%	1.024
25% Q1	0.975	10%	0.96
0% Min	0.943	5%	0.952
		1%	0.946
Range	0.118		
Q3-Q1	0.037		
Mode	0.975		

Extremes

Lowest	Obs	Highest	Obs
0.943(	7)	1.037(	60)
0.946(	82)	1.039(	20)
0.946(	41)	1.046(	102)
0.946(	10)	1.06(	54)
0.951(	108)	1.061(	28)

Fitted Distribution: Normal

Parameters		Goodness-of-Fit	
Mean (Mu)	0.99285593	Chi-Square	9.59857846
Std Dev (Sigma)	0.02515738	Df	10
		Pr > Chi-Square	0.47638814

Quantiles

Percent	Obs Quantile	Est Quantile
1.0	0.94600	0.93433
5.0	0.95200	0.95148
10.0	0.96000	0.96062
25.0	0.97500	0.97589
50.0	0.99100	0.99286
75.0	1.01200	1.00982
90.0	1.02400	1.02510
95.0	1.03200	1.03424
99.0	1.06000	1.05138

CAPABILITY

Variable=CF_VAR Calibration Factor Measurement Variance

Moments

N	118	Sum Wgts	118
Mean	0.000173	Sum	0.020471
Std Dev	0.000253	Variance	6.422E-8
Skewness	2.413302	Kurtosis	6.883897
USS	0.000011	CSS	7.514E-6
CV	146.0803	Std Mean	0.000023
T:Mean=0	7.436172	Prob>|T|	0.0000
Sgn Rank	3510.5	Prob>|S|	0.0000
Num ^= 0	118		
W:Normal	0.701532	Prob<W	0.000

Quantiles(Def=5)

100% Max	0.001444	99%	0.001089
75% Q3	0.000225	95%	0.000729
50% Med	0.000081	90%	0.000529
25% Q1	0.00001	10%	4E-6
0% Min	1E-6	5%	1E-6
		1%	1E-6
Range	0.001443		
Q3-Q1	0.000215		
Mode	1E-6		

Extremes

Lowest	Obs	Highest	Obs
1E-6(	96)	0.000729(	103)
1E-6(	85)	0.0009(	47)
1E-6(	81)	0.001024(	33)
1E-6(	61)	0.001089(	93)
1E-6(	39)	0.001444(	95)

Fitted Distribution: Gamma

Parameters		Goodness-of-Fit	
Threshold (Theta)	0	Chi-Square	15.0376603
Scale (Sigma)	0.00034697	Df	13
Shape (Alpha)	0.5	Pr > Chi-Square	0.30500763
Est Mean	0.00017348		
Est Std Dev	0.00024534		

Quantiles

Percent	Obs Quantile	Est Quantile
1.0	0.000001	0.00000003
5.0	0.000001	0.00000068
10.0	0.000004	0.00000274
25.0	0.000010	0.00001761
50.0	0.000081	0.00007892
75.0	0.000225	0.00022957
90.0	0.000529	0.00046937
95.0	0.000729	0.00066643
99.0	0.001089	0.00115104

CAPABILITY

Variable=BLANK Blank (ug)

Moments

N	116	Sum Wgts	116
Mean	0.428759	Sum	49.736
Std Dev	0.110549	Variance	0.012221
Skewness	0.466144	Kurtosis	0.404717
USS	22.73016	CSS	1.405425
CV	25.78351	Std Mean	0.010264
T:Mean=0	41.77216	Prob>|T|	0.0000
Sgn Rank	3393	Prob>|S|	0.0000
Num ^= 0	116		
W:Normal	0.965653	Prob<W	0.043

Quantiles(Def=5)

100% Max	0.755	99%	0.737
75% Q3	0.486	95%	0.644
50% Med	0.414	90%	0.587
25% Q1	0.3645	10%	0.296
0% Min	0.191	5%	0.242
		1%	0.21
Range	0.564		
Q3-Q1	0.1215		
Mode	0.402		

Extremes

Lowest	Obs	Highest	Obs
0.191(	77)	0.647(	79)
0.21(	37)	0.649(	93)
0.22(	24)	0.658(	78)
0.235(	53)	0.737(	97)
0.241(	10)	0.755(	60)

Fitted Distribution: Normal

Parameters		Goodness-of-Fit	
Mean (Mu)	0.42875862	Chi-Square	26.1244077
Std Dev (Sigma)	0.11054903	Df	9
		Pr > Chi-Square	0.00194938

Quantiles

Percent	Obs Quantile	Est Quantile
1.0	0.21000	0.17158
5.0	0.24200	0.24692
10.0	0.29600	0.28708
25.0	0.36450	0.35419
50.0	0.41400	0.42876
75.0	0.48600	0.50332
90.0	0.58700	0.57043
95.0	0.64400	0.61060
99.0	0.73700	0.68593

Fitted Distribution: Lognormal

Parameters		Goodness-of-Fit	
Threshold (Theta)	0	Chi-Square	22.1881827
Scale (Zeta)	-0.8806807	Df	9
Shape (Sigma)	0.26432587	Pr > Chi-Square	0.00830133
Est Mean	0.42923678		
Est Std Dev	0.11546932		

Quantiles

Percent	Obs Quantile	Est Quantile
1.0	0.21000	0.22412
5.0	0.24200	0.26835
10.0	0.29600	0.29540
25.0	0.36450	0.34681
50.0	0.41400	0.41450
75.0	0.48600	0.49540
90.0	0.58700	0.58162
95.0	0.64400	0.64025
99.0	0.73700	0.76662

Fitted Distribution: Gamma

Parameters		Goodness-of-Fit	
Threshold (Theta)	0	Chi-Square	20.4930817
Scale (Sigma)	0.02868257	Df	9
Shape (Alpha)	14.9484022	Pr > Chi-Square	0.01510167
Est Mean	0.42875862		
Est Std Dev	0.1108959		

Quantiles

Percent	Obs Quantile	Est Quantile
1.0	0.21000	0.21342
5.0	0.24200	0.26405
10.0	0.29600	0.29419
25.0	0.36450	0.34969
50.0	0.41400	0.41924
75.0	0.48600	0.49746
90.0	0.58700	0.57560
95.0	0.64400	0.62596
99.0	0.73700	0.72793

CAPABILITY

Variable=BK_VAR Blank Variance

Moments

N	118	Sum Wgts	118
Mean	0.006574	Sum	0.775781
Std Dev	0.007184	Variance	0.000052
Skewness	1.760734	Kurtosis	4.000298
USS	0.011139	CSS	0.006039
CV	109.276	Std Mean	0.000661
T:Mean=0	9.940685	Prob>|T|	0.0000
Sgn Rank	3510.5	Prob>|S|	0.0000
Num ^= 0	118		
W:Normal	0.820725	Prob<W	0.000

Quantiles(Def=5)

100% Max	0.04	99%	0.029584
75% Q3	0.009801	95%	0.021025
50% Med	0.004831	90%	0.015876
25% Q1	0.001089	10%	0.000225
0% Min	9E-6	5%	0.000081
		1%	9E-6
Range	0.039991		
Q3-Q1	0.008712		
Mode	0.000081		

Extremes

Lowest	Obs	Highest	Obs
9E-6(	2)	0.021316(	114)
9E-6(	1)	0.025281(	115)
0.000016(	3)	0.025281(	116)
0.000081(	6)	0.029584(	117)
0.000081(	5)	0.04(	118)

Fitted Distribution: Gamma

Parameters

Threshold (Theta)	0
Scale (Sigma)	0.00657442
Shape (Alpha)	1
Est Mean	0.00657442
Est Std Dev	0.00657442

Goodness-of-Fit

Chi-Square	8.52059788
Df	7
Pr > Chi-Square	0.2889302

Quantiles

Percent	Obs Quantile	Est Quantile
1.0	0.000009	0.00007
5.0	0.000081	0.00034
10.0	0.000225	0.00069
25.0	0.001089	0.00189
50.0	0.004831	0.00456
75.0	0.009801	0.00911
90.0	0.015876	0.01514
95.0	0.021025	0.01970
99.0	0.029584	0.03028

CAPABILITY

Low Range Duplicate Differences Squared

Moments

N	64	Sum Wgts	64
Mean	0.053862	Sum	3.447153
Std Dev	0.079998	Variance	0.0064
Skewness	2.133838	Kurtosis	4.775936
USS	0.588854	CSS	0.403185
CV	148.5255	Std Mean	0.01
T:Mean=0	5.38628	Prob>|T|	0.0000
Sgn Rank	1040	Prob>|S|	0.0000
Num ^= 0	64		

Quantiles(Def=5)

100% Max	0.376996	99%	0.376996
75% Q3	0.073261	95%	0.222784
50% Med	0.016276	90%	0.152881
25% Q1	0.003101	10%	0.0001
0% Min	1E-6	5%	1E-6
		1%	1E-6
Range	0.376995		
Q3-Q1	0.07016		
Mode	1E-6		

Extremes

Lowest	Obs	Highest	Obs
1E-6(	41)	0.195364(	19)
1E-6(	40)	0.222784(	51)
1E-6(	34)	0.245025(	33)
1E-6(	11)	0.312481(	60)
4E-6(	3)	0.376996(	56)

Fitted Distribution: Gamma

Parameters		Goodness-of-Fit	
Threshold (Theta)	0	Chi-Square	6.22198531
Scale (Sigma)	0.10772353	Df	6
Shape (Alpha)	0.5	Pr > Chi-Square	0.39878831
Est Mean	0.05386177		
Est Std Dev	0.07617204		

Quantiles

Percent	Obs Quantile	Est Quantile
1.0	0.000001	0.000008
5.0	0.000001	0.000212
10.0	0.000100	0.000851
25.0	0.003101	0.005469
50.0	0.016276	0.024504
75.0	0.073261	0.071275
90.0	0.152881	0.145725
95.0	0.222784	0.206908
99.0	0.376996	0.357367

CAPABILITY

Mid Range Duplicate Differences Squared

Moments

N	30	Sum Wgts	30
Mean	0.108874	Sum	3.266231
Std Dev	0.126293	Variance	0.01595
Skewness	1.029248	Kurtosis	-0.29855
USS	0.818157	CSS	0.462548
CV	115.9989	Std Mean	0.023058
T:Mean=0	4.721791	Prob>|T|	0.0001
Sgn Rank	232.5	Prob>|S|	0.0000
Num ^= 0	30		

Quantiles(Def=5)

100% Max	0.378225	99%	0.378225
75% Q3	0.196249	95%	0.368449
50% Med	0.043484	90%	0.335917
25% Q1	0.011025	10%	0.001717
0% Min	1E-6	5%	1E-6
		1%	1E-6
Range	0.378224		
Q3-Q1	0.185224		
Mode	0.011025		

Extremes

Lowest	Obs	Highest	Obs
1E-6(	3)	0.268324(	22)
1E-6(	2)	0.305809(	7)
0.000625(	13)	0.366025(	14)
0.002809(	26)	0.368449(	4)
0.005476(	25)	0.378225(	20)

Fitted Distribution: Gamma

Parameters

Threshold (Theta)	0
Scale (Sigma)	0.21774873
Shape (Alpha)	0.5
Est Mean	0.10887437
Est Std Dev	0.15397161

Goodness-of-Fit

Chi-Square	7.71422645
Df	7
Pr > Chi-Square	0.35846631

Quantiles

Percent	Obs Quantile	Est Quantile
1.0	0.000001	0.00002
5.0	0.000001	0.00043
10.0	0.001717	0.00172
25.0	0.011025	0.01105
50.0	0.043484	0.04953
75.0	0.196249	0.14407
90.0	0.335917	0.29456
95.0	0.368449	0.41824
99.0	0.378225	0.72237

CAPABILITY

Variable=RECOVERY Percent Recovery

Moments

N	77	Sum Wgts	77
Mean	98.61948	Sum	7593.7
Std Dev	3.574288	Variance	12.77554
Skewness	0.157161	Kurtosis	-0.02111
USS	749857.7	CSS	970.9408
CV	3.624323	Std Mean	0.407328
T:Mean=0	242.1132	Prob>|T|	0.0000
Sgn Rank	1501.5	Prob>|S|	0.0000
Num ^= 0	77		
W:Normal	0.988085	Prob<W	0.925

Quantiles(Def=5)

100% Max	108.7	99%	108.7
75% Q3	100.9	95%	104.8
50% Med	98.6	90%	102.7
25% Q1	96	10%	94.1
0% Min	90.6	5%	92.9
		1%	90.6
Range	18.1		
Q3-Q1	4.9		
Mode	98.1		

Extremes

Lowest	Obs	Highest	Obs
90.6(	32)	104.7(	64)
91.6(	42)	104.8(	77)
91.9(	37)	105.5(	39)
92.9(	46)	105.7(	56)
92.9(	35)	108.7(	52)

Fitted Distribution: Normal

Parameters		Goodness-of-Fit	
Mean (Mu)	98.6194805	Chi-Square	13.3495811
Std Dev (Sigma)	3.57428826	Df	16
		Pr > Chi-Square	0.6470463

Quantiles

Percent	Obs Quantile	Est Quantile
1.0	90.6000	90.3044
5.0	92.9000	92.7403
10.0	94.1000	94.0388
25.0	96.0000	96.2087
50.0	98.6000	98.6195
75.0	100.9000	101.0303
90.0	102.7000	103.2001
95.0	104.8000	104.4987
99.0	108.7000	106.9345

CORRELATION ANALYSIS

3 'VAR' Variables: CAL_FAC QCAPLUS QCAMINUS

Simple Statistics

Variable	N	Mean	Std Dev	Median
CAL_FAC	33	1.00258	0.02167	1.00200
QCAPLUS	33	39.17606	1.22829	39.37000
QCAMINUS	33	19.91212	1.00179	20.11000

Simple Statistics

Variable	Minimum	Maximum
CAL_FAC	0.94600	1.03900
QCAPLUS	36.60000	41.74000
QCAMINUS	17.88000	21.29000

Pearson Correlation Coefficients / Prob > |R| under Ho: Rho=0 / N = 33

	CAL_FAC	QCAPLUS	QCAMINUS
CAL_FAC	1.00000 0.0	-0.48737 0.0040	-0.18873 0.2929
QCAPLUS	-0.48737 0.0040	1.00000 0.0	0.77891 0.0001
QCAMINUS	-0.18873 0.2929	0.77891 0.0001	1.00000 0.0

Spearman Correlation Coefficients / Prob > |R| under Ho: Rho=0 / N = 33

	CAL_FAC	QCAPLUS	QCAMINUS
CAL_FAC	1.00000 0.0	-0.43770 0.0109	-0.10331 0.5672
QCAPLUS	-0.43770 0.0109	1.00000 0.0	0.74574 0.0001
QCAMINUS	-0.10331 0.5672	0.74574 0.0001	1.00000 0.0

CORRELATION ANALYSIS

2 'VAR' Variables: CAL_FAC CF_VAR

Simple Statistics

Variable	N	Mean	Std Dev	Median
CAL_FAC	118	0.99286	0.02516	0.99100
CF_VAR	118	0.0001735	0.0002534	0.0000810

Simple Statistics

Variable	Minimum	Maximum
CAL_FAC	0.94300	1.06100
CF_VAR	1E-6	0.00144

Spearman Correlation Coefficients / Prob > |R| under Ho: Rho=0 / N = 118

	CAL_FAC	CF_VAR
CAL_FAC	1.00000 0.0	-0.03556 0.7023
CF_VAR	-0.03556 0.7023	1.00000 0.0

CORRELATION ANALYSIS

2 'VAR' Variables: BLANK BK_VAR

Simple Statistics

Variable	N	Mean	Std Dev	Median
BLANK	118	0.43717	0.12739	0.42400
BK_VAR	118	0.00657	0.00718	0.00483

Simple Statistics

Variable	Minimum	Maximum
BLANK	0.19100	0.99300
BK_VAR	9E-6	0.04000

Spearman Correlation Coefficients / Prob > |R| under Ho: Rho=0 / N = 118

	BLANK	BK_VAR
BLANK	1.00000 0.0	-0.12820 0.1665
BK_VAR	-0.12820 0.1665	1.00000 0.0

CAPABILITY

Variable=QCAPLUS

Moments

N	33	Sum Wgts	33
Mean	39.17606	Sum	1292.81
Std Dev	1.228291	Variance	1.5087
Skewness	-0.20089	Kurtosis	-0.38139
USS	50695.48	CSS	48.27839
CV	3.135311	Std Mean	0.213818
T:Mean=0	183.2215	Prob>|T|	0.0000
Sgn Rank	280.5	Prob>|S|	0.0000
Num ^= 0	33		
W:Normal	0.981238	Prob<W	0.858

Quantiles(Def=5)

100% Max	41.74	99%	41.74
75% Q3	40.06	95%	41.15
50% Med	39.37	90%	40.58
25% Q1	38.52	10%	37.56
0% Min	36.6	5%	36.87
		1%	36.6
Range	5.14		
Q3-Q1	1.54		
Mode	36.6		

Extremes

Lowest	Obs	Highest	Obs
36.6(	9)	40.48(	10)
36.87(	8)	40.58(	3)
37.51(	31)	40.64(	19)
37.56(	29)	41.15(	1)
37.58(	27)	41.74(	4)

Fitted Distribution: Normal

Parameters		Goodness-of-Fit	
Mean (Mu)	39.1760606	Chi-Square	2.0733325
Std Dev (Sigma)	1.22829134	Df	3
		Pr > Chi-Square	0.55732659

Quantiles

Percent	Obs Quantile	Est Quantile
1.0	36.6000	36.3186
5.0	36.8700	37.1557
10.0	37.5600	37.6019
25.0	38.5200	38.3476
50.0	39.3700	39.1761
75.0	40.0600	40.0045
90.0	40.5800	40.7502
95.0	41.1500	41.1964
99.0	41.7400	42.0335

CAPABILITY

Variable=QCAMINUS

Moments

N	33	Sum Wgts	33
Mean	19.91212	Sum	657.1
Std Dev	1.001795	Variance	1.003592
Skewness	-0.44935	Kurtosis	-0.94757
USS	13116.37	CSS	32.11495
CV	5.031079	Std Mean	0.17439
T:Mean=0	114.1815	Prob>|T|	0.0000
Sgn Rank	280.5	Prob>|S|	0.0000
Num ^= 0	33		
W:Normal	0.923324	Prob<W	0.027

Quantiles(Def=5)

100% Max	21.29	99%	21.29
75% Q3	20.51	95%	21.24
50% Med	20.11	90%	21.2
25% Q1	19.02	10%	18.64
0% Min	17.88	5%	18.11
		1%	17.88
Range	3.41		
Q3-Q1	1.49		
Mode	19.83		

Extremes

Lowest	Obs	Highest	Obs
17.88(	30)	21.11(	4)
18.11(	29)	21.2(	7)
18.35(	22)	21.22(	24)
18.64(	9)	21.24(	19)
18.65(	15)	21.29(	1)

Fitted Distribution: Normal

Parameters		Goodness-of-Fit	
Mean (Mu)	19.9121212	Chi-Square	7.97620782
Std Dev (Sigma)	1.00179451	Df	3
		Pr > Chi-Square	0.04650599

Quantiles

Percent	Obs Quantile	Est Quantile
1.0	17.8800	17.5816
5.0	18.1100	18.2643
10.0	18.6400	18.6283
25.0	19.0200	19.2364
50.0	20.1100	19.9121
75.0	20.5100	20.5878
90.0	21.2000	21.1960
95.0	21.2400	21.5599
99.0	21.2900	22.2426

Appendix 4

Method E128.0 for Adsorbable Organic Halide

ADSORBABLE ORGANIC HALIDES IN PULP MILL EFFLUENT

1. Scope and Application

1.1 This method describes the procedure for measuring adsorbable organic halide (AOX) in bleached kraft mill effluent. In these effluents, the AOX present is almost exclusively organically bound chlorine even though the method is sensitive to organic bromine and iodine as well.

1.2 The term organic chlorine is used throughout this method, and includes all organically bound halogens.

1.3 This method is designed to give results consistent with the Scandinavian Pulp, Paper and Board Testing Method SCAN 9:89. This method determines organic chlorine in both dissolved and suspended material.

1.4 This method is applicable to samples with an AOX concentration range of 25 to 400 µg/L of effluent as submitted, measured as chloride. Samples with higher AOX concentrations must be diluted prior to analysis.

2. Summary of Method

2.1 This method consists of three steps.

2.1.1 The adsorption of organic compounds in a 100 mL sample onto granular activated carbon (GAC) and the displacement of adsorbed inorganic chloride with nitrate ions.

2.1.2 The combustion of the GAC and suspended material to convert all the organic chlorine to hydrogen chloride.

2.1.3 A titration of resulting chloride with microcoulometrically generated silver ion.

3. Interferences

3.1 Organically bound chlorine contamination of sample, reagent water, and GAC will cause elevated background, and greater variation of the background. Some sources of organically bound chlorine are volatile chlorinated laboratory solvents, and halogenated compounds present in improperly prepared reagent waters.

3.2 Bound chlorine present in membrane filters can cause an increase in the magnitude and variation of the background.

3.3 To avoid contamination, all analyses should be performed in an environment where chlorinated solvents can be excluded. All material used in the analysis should be stored in a desiccator over activated carbon.

3.4 Inorganic chloride can be detected when present in the diluted sample in concentrations greater than 1.0 mMole (5.8 mg/100mL as sodium chloride; 3.5 mg/100 mL chloride).

3.5 When the sample has a high concentration of dissolved organic carbon, the GAC can become saturated before adsorbing all the organic halide present, leading to low recoveries.

4. Sample Collection, Preservation, and Handling

4.1 Samples must be collected in 500 mL polyethylene bottles and filled with no head space. Samples must be acidified with nitric acid to a pH less than 2.1 and greater than 1.5.

4.2 If the sample contains active chlorine[1], add one crystal of sodium sulphite to neutralize the chlorine. It is important that the sample be acidified prior to the addition of sodium sulphite, and that the addition is recorded.

4.3 A trip blank of ASTM Type II reagent water or better, acidified to pH 1.5 to 2.1 with nitric acid, must be prepared.

4.4 Samples must be iced or refrigerated at 4°C upon collection and maintained at 4°C until analysis.

4.5 Samples must be analyzed within 14 days of sampling.

5. Safety

5.1 The laboratory maintains material safety data sheets (MSDS) for all chemicals involved in this method. This material is readily available to all personnel involved in the chemical analysis.

5.2 Additional references to laboratory safety have been identified for the information of the analysts.

6. Apparatus and Materials

6.1 Sampling Equipment.

6.1.1 Sampling bottle - 500 mL polyethylene bottle with screw cap.

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[1] Most effluents will contain no active chlorine. To determine if any is present, add one crystal of potassium iodide, then two drops of a 1% starch solution to 10 mL of the effluent. An immediate change in colour to blue, upon addition of the starch solution, indicates that active chlorine is present.

6.1.2 Nitric acid - 50% nitric acid to acidify the sample. One 5 mL ampoule provided by the laboratory added to the 500 mL sample usually achieves the desired pH.

6.1.3 pH Meter - pH meter accurate to ± 0.1 pH units.

6.1.4 Starch solution - 1% starch solution in reagent water.

6.1.5 Sodium sulphite - ACS reagent grade (crystal).

6.1.6 Potassium iodide - ACS reagent grade (granular).

6.1.7 Reagent water - ASTM Type II or better for trip blank.

6.1.8 Cooler and ice.

6.1.9 Glass vial or test tube.

6.2 Glassware.

6.2.1 Transfer pipettes, 5.00 mL, 10.00 mL, and 20.00 mL.

6.2.2 Syringes, 10.0 µL, 25µL and 50 µL gas tight.

6.2.3 Volumetric flasks, 50.00 mL and 100.00 mL.

6.2.4 Filtering apparatus, sintered glass filter supports for 25 mm membrane filters, vacuum manifold.

6.2.5 Conical flasks, 250 mL with ground glass stopper.

6.3 Equipment.

6.3.1 Orbital Stirrer, adjustable to > 120 cycles per second.

6.3.2 Vacuum source, suitable for vacuum filtration.

6.3.3 pH Meter, accurate to ± 0.01 pH units, and associated calibration buffers.

6.3.4 Polycarbonate membrane filters, 0.40 µm pore size, 25 mm diameter.

6.3.5 Measuring scoop, designed to deliver 40 mg of GAC.

6.3.6 Analytical balance, capable of weighing ± 0.0001 g.

6.3.7 AOX Microcoulometric System, capable of determining 0.1 to 50 µg Cl. This includes any additional apparatus and chemicals specified by the manufacturer (i.e. electrode and electrolytes).

6.4 Chemicals.

6.4.1 Sodium chloride - ACS reagent grade.

6.4.2 Sodium nitrate - ACS reagent grade.

6.4.3 Sodium bicarbonate - ACS reagent grade.

6.4.4 Silver nitrate - ACS reagent grade.

6.4.5 2,4,6-Trichlorophenol - >98% purity.

6.4.6 2-Chlorobenzoic acid - >98% purity.

6.4.7 Nitric acid - 1.40 g/mL.

6.4.8 Methanol - distilled in glass, chlorine free.

6.4.9 Reagent water - ASTM Type II (or better) reagent water.

6.4.10 Granular activated carbon, zero chlorine.

7. Reagents

7.1 All aqueous reagent solutions are prepared using ASTM Type II (or better) reagent water. Solutions in methanol are prepared using distilled in glass, chlorine free methanol.

7.2 Dilute nitric acid - 1.4 mL of nitric acid diluted to 1000 mL with reagent water.

7.3 Nitrate solution - dissolve 17 g of sodium nitrate in 1000 mL of dilute nitric acid.

7.4 Washing solution - dilute 100 mL of nitrate solution to 1000 mL with reagent water.

7.5 Sodium chloride solution - dissolve 0.1200 g sodium chloride in 200.0 mL reagent water.

7.6 Silver nitrate solution - dissolve 0.1700 g silver nitrate in 100.0 mL reagent water.

7.7 2,4,6-Trichlorophenol solution - dissolve 0.1857 g 2,4,6-trichlorophenol in 100.0 mL methanol (1.000 µg Cl/µL).

7.8 2-Chlorobenzoic acid - dissolve 0.1102 g of 2-chlorobenzoic acid in 50.0 mL methanol (0.500 µg Cl/µL).

7.9 2,4,6-Trichlorophenol quality control A (QCA) solution - dissolve 0.5520 g of 2,4,6-trichlorophenol in 100.0 mL methanol.

7.10 2,4,6-Trichlorophenol quality control B (QCB) solution - dissolve 0.1380 g of 2,4,6-trichlorophenol in 100.0 mL of methanol.

8. Sample Adsorption[1]

8.1 All samples are analyzed at least twice. The dilution used for one determination is double that of the other.

8.2 This method provides for the analysis of the organically bound chlorine in suspended material. Samples must be shaken vigorously to suspend the particulate material prior to aliquots being taken.

8.3 Dilute the sample to the working range 25-400 µg/L of the instrument (25-400 µg/L AOX), using dilute nitric acid.[2] All dilutions are performed using aliquots of not less than 5 mL into dilute nitric acid. When dilutions of greater than 1 to 10 are required, the dilution must be done in multiple stages, each no more than 1 to 10. All but the final dilutions, are performed in volumetric flasks. Final dilutions are performed in 250 mL conical flasks. Typical bleached kraft mill effluents require a dilution of either 10 mL or 20 mL to 100 mL followed by dilutions of 5 mL and 10 mL[2] to 100 mL.

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1 Requirements for an organic chlorine free laboratory environment, specified in Sections 3.1 and 3.3 must be strictly adhered to.

2 This method requires analysis at two dilutions, one double the other.

8.4 All dilutions are recorded and the final effective volume of the sample is calculated as:

effective volume = dilution 1 x dilution 2...x100 mL.

8.5 Five mL of nitrate solution and 40 mg of GAC (using scoop specified in Section 6.3) are added to diluted sample in the 250 mL conical flasks. Flasks are then capped and agitated by orbital shaker for not less than 1 hour, at a rate greater than 120 cycles per second.

8.6 The contents of the 250 mL flask are filtered, collecting the GAC and insoluble material on a 0.40 µm polycarbonate filter (25 mm diameter). The flask is rinsed with small aliquots of wash solution (the combined aliquots totalling 25 mL). The interior wall of the filter unit is rinsed so that all the particulate material is collected on the membrane filter. Great care must be taken not to draw large volumes of air over the filter bed.

8.7 A minimum of two method blanks (dilute nitric acid) must be analyzed per day. The method blank is prepared using only dilute nitric and nitrate solution, with the GAC, in the adsorption step. The GAC is collected by filtration using the same method and techniques as the samples.

8.8 One sample fortified with 2-chlorobenzoic acid (standard addition) must be analyzed per day (see Section 13.4). The fortified sample is prepared by adding 20 µL of 2-chlorobenzoic acid solution to the final dilution of the sample to the 250 mL conical flask, prior to the addition of GAC.

9. Cleanup

Not applicable for this method.

10. Sample Combustion and Chloride Determination by Microcoulometry.

10.1 Twenty µL of the test titrations of sodium chloride solution (see Section 7.5) injected directly into the microcoulometric cell are performed to determine the coulometer operating parameters.

10.2 At daily startup and after routine cell maintenance (changing electrolyte and polishing working electrode), 10 µL of 2,4,6-trichlorophenol solution, injected directly into the sample boat must be analyzed (two analysis after daily startup). Recovery of AOX (as chloride) must all be within the range of 95 to 105%, with a standard deviation no greater than 3%.

10.3 The filter membrane, containing the GAC and filtered material, is transferred quantitatively to the sample boat, and is combusted at 950°C under an atmosphere of oxygen, in the pyrolysis oven. The microcoulometer and cell are operated in accordance with the manufacturer specifications. Any exceptions must be noted. Results are recorded as µg chloride detected. This is the instrument AOX.

11. Calibration

11.1 A calibration curve over the full operating range of the method (2.5 to 40 µg AOX as chloride) must be developed. Aliquots of 2,4,6-trichlorophenol solution of 5, 10, 15, 25, and 40 µL are directly injected into the sample boat and analyzed. Calibration curves must be run after any instrument reconfiguration and after major maintenance (i.e. pyrolysis tube and/or packing replacement, electrode replacement)[1].

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1 After cell maintenance such as electrode replacement, the analyst may wish to verify cell and microcoulometer operation with direct injection of sodium chloride solution into the cell. These analyses do not constitute calibration.

11.2 Daily calibration injections of 10 µL 2,4,6-trichlorophenol solution (discussed in 10.2) are used for routine calibration. The calibration factor is the mean of all results divided by the amount determined (approximately 10 µg AOX as chloride).

12. Calculation

12.1 The daily calibration factor[1] is calculated as the mean of the calibration determinations (Section 11.2).

12.2 The blank[2] AOX is calculated as the mean of the blank determinations (Section 8.7).

12.3 Calibrated AOX[3] in µg is calculated using the formula:

$$\text{Calibrated AOX} = \frac{\text{Instrument AOX} - \text{Blank AOX}}{\text{calibration factor}}$$

12.4 The AOX concentration of each dilution of the sample (Section 8.1) is calculated using the formula:

$$\text{AOX concentration} = \frac{\text{Calibrated AOX (µg)}}{\text{effective volume (mL) (Section 8.4)}}$$

Sample AOX concentration is the average of the AOX concentrations of each dilution[4]. This result in

---

1 The calibration factor must be within the range of 0.95 to > 1.05 with a standard deviation of less than 0.03.

2 The blank must be less than 1.0 µg AOX with a standard deviation less than 0.3 µg.

3 Instrument AOX must be within the range of 2.5 to 40 µg.

4 The AOX concentrations of both dilutions of a sample must agree within 10%: $-10 \leq \frac{100 \times 2x(A-B)}{A+B} \leq 10$

A = AOX Concentration of dilution 1

B = AOX Concentration of dilution 2

µg/mL requires no conversion factor to be expressed in mg/L. If all of the specified criteria (see footnotes) have not been met, the results cannot be accepted.

12.5 The 2-chlorobenzoic acid spike recovery is calculated as follows.

$$\text{Recovery } \% = 100 \times \frac{(C-D)}{EXF}$$

where C = calibrated AOX for spike sample.

D = AOX concentration of sample spiked multiplied by the effective volume of the spike sample.

E = concentration of 2-chlorobenzoic acid solution in µg AOX per µL.

F = volume of 2-chlorobenzoic acid solution, in µL, added.

The percent recovery of 2-chlorobenzoic acid as AOX must be within the range of 90 to 105% and must be reported with results.

13. Quality Assurance/Quality Control (QA/QC)

13.1 A daily calibration factor is calculated from the recovery factors of multiple 10.0 µL injections of trichlorophenol solutions directly into the sample boat (Section 10.2). The mean of the calibration factors must be no less than 0.95 and no more than 1.05 with a standard deviation of no more than 0.03.

13.1.2 QCA and QCB Analysis. QCA and QCB solutions are analyzed daily (10 µL injection directly into sample boat). The calibrated results are plotted on control charts. Control limits will be set when sufficient data is generated.

13.1.3 Full calibration curves must be developed after all major maintenance (Section 11.1). The slope of this curve must not be less than 0.95 and no more than 1.05, and a correlation factor of no less than 0.9995 must be achieved.

13.1.4 In the event of failure of either Section 13.1.1 or 13.1.2, any data generated must be rejected and the instrument must be brought back into control before any further analysis.

13.2 Analysis of Method Blanks.

13.2.1 At least two method blanks, as described in Section 8.7, must be analyzed per day. Any single determination over 1.0 µg or a spread of greater than 0.3 µg indicate that the method is out of control[1]. Steps must be taken to identify and remove the source of contamination before continuing with analysis.

13.3 Analysis of Duplicates and Replicates.

13.3.1 A minimum of one randomly selected sample per ten samples, or one per day (whichever is greater), is analyzed in duplicate. These results will be used to estimate the precision of the method. As data is generated precision limits will be determined.

13.3.2 All samples are analyzed at two different dilutions (Section 8.3). The two results must agree to within 10% or be rerun.

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1 A blank must be the first method determination of the day, after test titrations and calibration determinations. High results may occur. If so, repeat the blank determination. If the second result falls within the acceptance range, disregard the first result, and continue analysis.

13.4 Analysis of Samples Fortified with 2-Chlorobenzoic Acid.

13.4.1 One dilution of each sample, randomly selected for duplicate analysis, is fortified with 20 µL of 2-chlorobenzoic acid solution and analyzed (Section 8.8). The recovery of AOX (Section 12.3) must be no less than 90% and no greater than 105%.

13.5 Analysis of Standard Reference Material.

13.5.1 The diverse nature and instability of the organic chlorine containing compounds in pulp mill effluents precludes the use of any standard reference material for pulp mill effluent AOX analysis.

13.6 Analysis of Reagent and Materials Used in Analysis.

13.6.1 Every lot of all materials and reagents used in the method are analyzed for chlorine prior to their use in AOX analysis.

13.7 Recording and Charting of QA/QC Data.

13.7.1 Current records and charts of all QA/QC charts will be maintained and made available to clients upon request.

13.8 General Laboratory Practices.

13.8.1 The working electrode is kept polished (sodium bicarbonate). If any discolouration or coating is observed during operation, analysis is stopped and the electrode is polished and the cell electrolyte is changed.

13.8.2 Analysis is only performed when the cell electrolyte is clear. When the electrolyte becomes cloudy, the cell is rehabilitated as above.

13.8.3 Cell electrolyte solution is prepared in large batches (lots) and tested before use. Uniformity of the batch is assumed. Changing cell electrolyte should not change cell efficiency.

13.8.4 Test titrations are performed after cell rehabilitation to oxidize trace amounts of impurity which may be present, and to ensure that the cell is operating correctly.

13.8.5 The outlet of the pyrolysis tube is visually inspected daily for soot or discolouration.

13.8.6 Joints are carefully inspected in the transfer/dehydration system.

13.8.7 Dilute nitric acid, nitrate solution and washing solutions are prepared in large lots to ensure uniformity of error.

13.8.7 New lots of GAC and membrane filter are tested for halide content prior to use in analysis.

14. Method Performance

Evaluation will be completed when sufficient data is available.

15. References

15.1 Scandanavian Pulp, Paper and Board Testing Committee, Standard Method SCAN-W 9:89, (1989).

15.2 DIN: DIN 38409H 14 Summarische Wirkungs and Stoffkenngro Ben (Gruppe H), Bestimmung der adsorbierbaren organisch gebundenen Haloger (AOX), Beuth-Verlag, Berlin (1985).

15.3 Methods for the Examination of Water and Waste water. Method 506 Organic Halogen (Dissolved). American Public Health Association, Washington, D.C. (1989).

15.4 L. Bauman and M.K. Stenstrom, Observations of Reaction between Organohalides and Sulfite, Environ. Sci. and Technol. 23, 232 (1989).

15.5 ASTM Standard Specification for Reagent Water. D1193-77 (Reapproved 1983).

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